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Inhibiting properties of imidazole and 2-methylimidazole as corrosion inhibitor for mild steel in hydrochloric acid

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ABSTRACT

The inhibition effect of imidazole and 2-methylimidazole on the corrosion of mild steel in 1N hydrochloric acid 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 in 1N hydrochloric acid. But higher temperature at 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 inhibitor on the mild steel surface has been found to obey Temkin's adsorption isotherm. Potentiostatic polarization results reveal that imidazole and 2-methyl imidazole act as mixed type inhibitor. The values of activation energy (Ea), free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH), and entropy of adsorption (ΔS) were also calculated.

Key words: Mild Steel; Hydrochloric acid; Corrosion inhibition; Temkin's adsorption isotherm; Potentiostatic polarization; imidazole; 2-methylimidazole

INTRODUCTION

Corrosion is a prevailing destructive phenomenon in science and technology. It is an complex subject and difficult to analyze due to the large number of variables involved. However, a comprehensive survey of the existing literature reveals that enormous work has been directed at understanding corrosion phenomena and particular attention has been given to the prevention of metallic corrosion by the use of chemical inhibitors in metal – corrodent systems[1-3].

Iron and its alloys are extensively used in many engineering applications in various environments especially in inorganic and organic acid environments because of their excellent combination of properties. Concentrated mineral acids are used extensively in pickling, cleaning, descaling and oil well aciding 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, Oxygen and nitrogen atoms are good corrosion inhibitors for the acidic dissolution of metals[6-10].

Hence imidazole and 2-methylimidazole have been chosen as inhibitors for mild steel in hydrochloric acid medium. The effect of difference in the molecular structure of the inhibitors and mechanism has also been studied by mass loss method and polarization technique.

It is aimed to predict the corrosion rate; inhibition efficiency and surface coverage on mild steel by absorbed imidazole and 2-methylimidazole at various temperatures and the thermodynamic feasibility such as activation energy (Ea), free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH), and entropy of adsorption (ΔS) were also calculated. The adsorption characteristic of imidazole and 2-methylimidazole 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 as shown below. The surface of specimens were polished with emery papers ranging from 110 to 410 grades and degreased with trichloroethylene specimens were dried and stored in vacuum desiccators containing siligagel and then initially weighed in an electronic balance. After that the specimens were suspended with the help of PTFE, threads and glass rod in 100ml beaker containing 1N hydrochloric acid in presence and absence of inhibitors. The specimens were removed after 4hours exposure period, washed with water to remove any corrosion products and finally washed with acetone. After that they were dried and reweighed. Mass loss measurements were carried out in 1N hydrochloric acid with imidazole and 2-methylimidazole in the concentration range of 0.1 % to 0.5% as inhibitors and the temperature between 303 K and 333 K for an immersion period of 4 hours. All the solutions were prepared with AR grade chemicals in double distilled water. Mass loss measurements were performed as per ASTM method described previously[11–14].

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 the working electrode. The saturated calomel electrode and the platinum foil were used as reference and counter electrodes respectively. The potentiostatic polarization measurement was carried out using BAS – 100 A model instrument. The potential of the test electrode was measured with respect to SCE and platinum electrode was used as auxiliary electrode and the experiment were carried out at 303K to333K.

RESULTS AND DISCUSSION

Mass loss studies

Table 1 shows the value of inhibition efficiency [IE%] surface coverage (è) and corrosion rate obtained at different concentration of the inhibitors in 1N hydrochloric acid solutions 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[15-17].

$$\mathrm{IE\%} = \frac{\mathrm{Wu\text{-}Wi}}{\mathrm{Wu}} \times 100 \qquad \text{...(1)}$$

$$\theta = \frac{\mathrm{Wu\text{-}Wi}}{\mathrm{Wu}} \qquad \text{...(2)}$$

where Wu and Wi are the corrosion rates for mild steel in the absence and presence of inhibitor respectively at the same temperature.

It could be seen from the table that the addition of inhibitor to the acid has reduced the corrosion rate. The inhibition efficiency increased with increase in concentration of inhibitors and increased with temperature from 303 K to 318 K and then decreased. The values of the corrosion rate and inhibition efficiency of the inhibitors are known to depend on the molecular structure of the inhibitors. The maximum inhibition efficiency of imidazole and 2-methyl imidazole was found to be 96.68% and 97.51% respectively in 1N hydrochloric acid at 0.5% of inhibitor concentration at 318K.

Thermodynamic / Kinetic Consideration

Table 2 shows that the calculated values of activation energy (Ea) and free energy of absorption (ΔGads) for mild steel corrosion in 1N hydrochloric acid with and without inhibitors at 303 to 333K. Energy of activation (Ea) was calculated from the slopes of plots of log p versus 1/T in fig 1&2 and also calculated from Arrhenius equation[18-20].

$$\log P_2/P_1 = Ea/2.303\ R\ [1/T_1 - 1/T_2] \qquad \text{...(3)}$$

where P_1 and P_2 are the corrosion rates at

Table 1: Calculated corrosion rate, inhibition efficiency (I.E. %) and surface coverage (q) for Imidazol and 2-methylimidazole from mass loss studies in 1N Hydrochloric Acid

Temperature (K)	Con. of Inhibitor (%) (mmpy)	Imidazol			2-Methyl imidazole		
		Corrosion Rate	Surface coverage (θ)	Inhibition Efficiency (%)	Corrosion Rate (mmpy)	Surface coverage (θ)	Inhibition Efficiency (%)
303	Blank	15.0000	-	-	15.0000	-	-
	0.1	7.2814	0.5146	51.46	6.0183	0.5987	59.87
	0.2	5.7954	0.6140	61.40	5.4982	0.6334	63.34
	0.3	4.7552	0.6833	68.33	4.5675	0.6955	69.55
	0.4	4.3837	0.7080	70.80	4.2351	0.7176	71.76
	0.5	3.5664	0.7626	76.26	3.3255	0.7783	77.83
318	Blank	371.3526	-	-	371.3526	-	-
	0.1	17.7577	0.9523	95.23	16.5689	0.9553	95.53
	0.2	13.0768	0.9647	96.47	14.0086	0.9622	96.22
	0.3	12.9282	0.9651	96.51	11.2936	0.9695	96.95
	0.4	12.7796	0.9657	96.57	10.4020	0.9719	97.19
	0.5	12.3338	0.9668	96.68	9.2132	0.9751	97.51
333	Blank	507.9165	-	-	507.9165	-	-
	0.1	60.6290	0.8806	88.06	58.5745	0.8846	88.46
	0.2	55.5022	0.8907	89.07	52.1287	0.8973	89.73
	0.3	51.1185	0.8993	89.93	49.0265	0.9034	90.34
	0.4	48.2646	0.9049	90.49	44.6534	0.9120	91.20
	0.5	42.9150	0.9155	91.55	41.2417	0.9188	91.88

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

inhibitor	Concentration of inhibitor (%)	Ea (from eqn,1) KJ/Mole	Ea (from plot) KJ/Mole	ΔG_{ads} KJ/Mole			ΔH KJ/ mole	ΔS KJ/ mol/k
				303K	318K	333K		
Imidazole +1NHCl	Blank	18.384	19.210	-	-	-	93.52	-
	0.1	72.086	72.596	-16.06	-24.63	-23.03	54.29	0.2321
	0.2	84.086	83.681	-15.34	-23.54	-21.37	58.20	0.2389
	0.3	80.702	82.789	-15.09	-22.58	-20.51	61.44	0.2460
	0.4	64.380	65.369	-14.65	-21.86	-19.89	59.10	0.2372
	0.5	57.623	56.158	-14.80	-21.36	-19.63	64.59	0.2529
2-methyl Imidazole +1NHCl	Blank	18.384	19.210	-	-	-	93.52	-
	0.1	74.129	75.247	-16.91	-24.80	-23.13	58.65	0.2830
	0.2	77.139	78.538	-15.54	-23.42	-21.57	57.92	0.2909
	0.3	86.184	85.458	-15.26	-22.94	-20.64	61.64	0.2957
	0.4	85.527	86.625	-15.31	-22.44	-20.13	60.89	0.2992
	0.5	87.986	89.288	-14.18	-22.18	-19.75	65.76	0.2990

Table 3: Electrochemical polarization parameters for the corrosion behaviour of mild steel in1N Hydrochloric acid with and without Imidazole and 2-Methylimidazole (At room temperature)

Concentration of inhibitor (%)	1N Hydrochloric acid with Imidazole					1N Hydrochloric acid with 2-Methylimidazole				
	E_{corr} Vs SCE (mv)	I_{corr} μA/ cm^2	Tafel constant mv/decade		IE (%)	E_{corr} Vs SCE (mv)	I_{corr} μA/ cm^2	Tafel constant mv/decade		IE (%)
			b_a	$-b_c$				b_a	$-b_c$	
Blank	-495	110	60	80	—-	-500	550	50	45	-
0.1	-505	95	45	30	13.63	-525	440	55	40	20.00
0.2	-515	90	50	65	18.18	-490	350	30	90	36.36
0.3	-525	80	90	55	27.27	-495	300	40	35	45.45
0.4	-510	70	55	50	36.36	-495	250	25	45	54.54
0.5	-515	50	55	45	54.54	-490	200	20	30	63.63

temperatures T_1 and T_2 respectively. Ea value was found to be 18.384KJ/mole in 1N hydrochloric acid at 318K to 333 K. The Ea values for 1N hydrochloric acid containing inhibitors are found to be higher than that of without inhibitors. These higher values of Ea indicate the physical adsorption of the inhibitors on metal surface[31-32] and also indicate that besides, adsorption of these inhibitors increases the activation energy of the corrosion process. The Ea values are calculated from the slopes of Arrhenius plot and by using equation-3 are approximately almost similar.

The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated from the following equation [23].

$$\Delta G\ (ads) = -RT\ \ln\ (55.5\ K) \qquad ...(4)$$

Where K is given by

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

Where θ is surface coverage on the metal surface ,C is concentration of inhibitor in mole/lit and K is equilibrium constant. 55.5 is concentration of water (mol./lit)

The negative values of (ΔG_{ads}) indicated the spontaneous adsorption of the inhibitors. 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}) indicating that inhibitors is physically adsorbed on the metal surface [24, 25].

The free energy of adsorption (ΔG_{ads}) of imidazole and 2-methyl imidazole can be calculated from the equation (4) at 303K to 333K, while the enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) were also calculated from the following equations[26].

$$\Delta H^0 = Ea\text{-}RT \qquad ...(6)$$

$$\Delta G^0 = \Delta H^0 - T\ \Delta S^0 \qquad ...(7)$$

Table 2 shows thermodynamic data obtained in this study .It could be seen from the table the activation energy increases linearly with increasing efficiency of the inhibitor.

Ideally, a corrosion inhibitor is a substance that greatly increases the activation energy of corrosion. The negative values of (ΔG_{ads}) indicate the spontaneous adsorption of the inhibitor on the surface of mild steel. It's also observed that (ΔS)

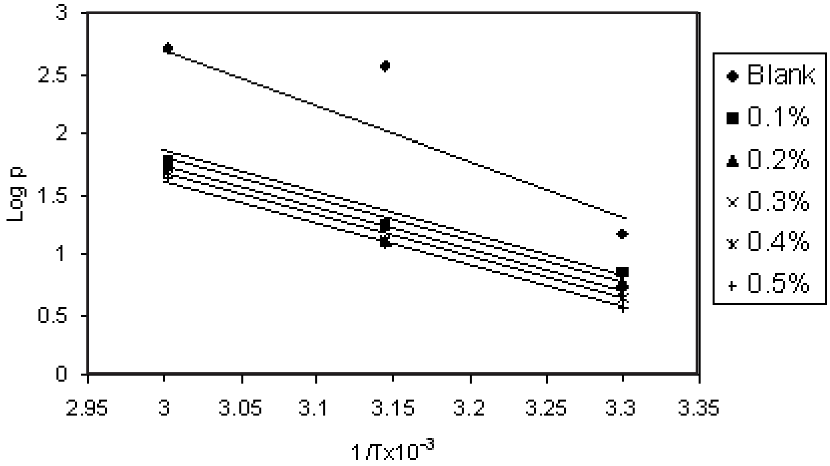

Fig. 1: Arrhenius Plot for Corrosion in 1N Hydrochloric acid with Imidazole

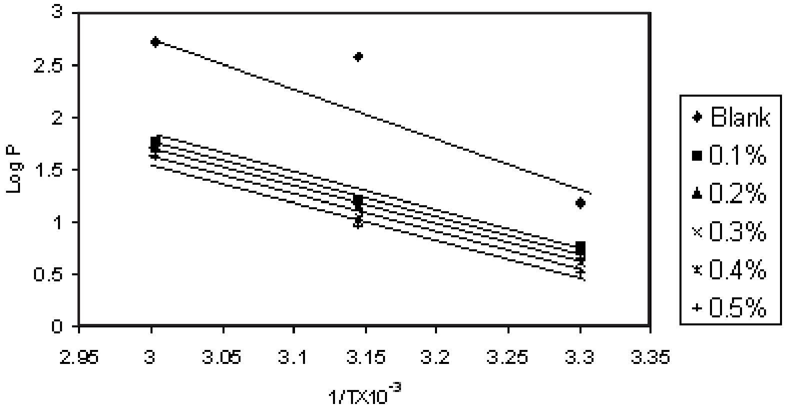

Fig. 2: Arrhenius Plot for Corrosion in 1N Hydrochloric acid with 2- Methylimidazole

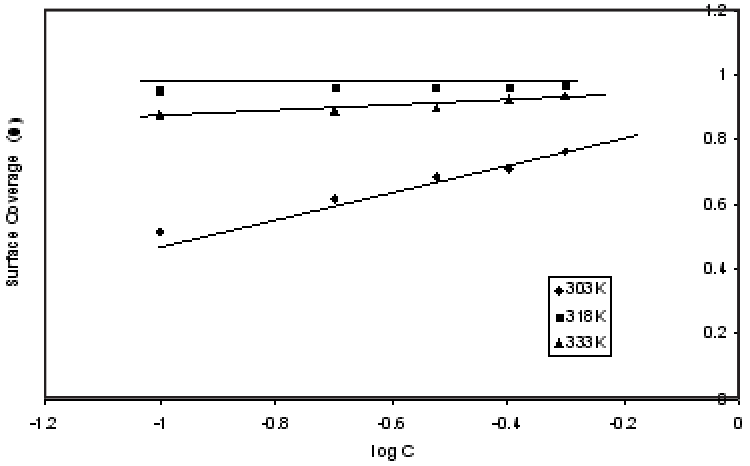

Fig. 3: Tempkin's adsorption isotherm for corrosion behaviour of mild steel in 1N hydrochloric acid with imidazole

increases with increasing efficiency of the inhibitors. This is opposite to that we expect, since the adsorption is an exothermic process and is always accompanied by a decrease in entropy. Ateya et. Al. [27] have described this situation as due to the adsorption of the organic compound, which is accompanied by desorption of water molecules from the surface. While the adsorption process is believed to be exothermic and associated with a decrease in entropy of the solute, the opposite is true for the solvent. Therefore, this gain in entropy that accompanied the substitutional adsorption process is attributed to the increase in solvent entropy.

Adsorption isotherms

The electrochemical process on the metal surface are likely to be closely to the adsorption of the inhibitors [28] and the adsorption is known to depend on the chemical structure of the inhibitors [29-31]. The adsorption of the inhibitors molecules from aqueous solutions can be regarded as quasi-substitution proceess[29] between the organic compound in the aqueous phase, org $(_{aq})$ and water molecules at the electrode surface, H_2O $(_s)$.

$$\text{Org}\ (_{aq}) + x\ H_2O\ (_s) = \text{org}(_{aq}) + x\ H_2O\ (_s).$$

where x (the size ratio) is the number of water molecules displaced by one molecule of inhibitor.

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The most frequently used are those of Langmuir, Frumkin, Parsons, Temkin , Flory –huggins and Bockris –Swinkels [32-35]. All these isotherms are of the general form:

$$f(\theta,x)\ \exp(-a\ \theta) = K\ C$$

where f (θ,x) is the configurational factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm[36].

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. The plot of surface coverage (θ) obtained by mass loss method versus log C at different concentrations of the inhibitors shows a straight line indicating that the adsorption of the inhibitor from acid on mild steel surface follows the Temkin's adsorption isotherm[27].This also points out that the corrosion inhibition by these compounds being a result of their adsorption on the metal surface.Figs.3 and 4 show the Temkin's adsorption isotherm plots for imidazole and 2-methyl imidazole.

Potentiostatic polarization studies

The Polarization behavior of mild steel functioning as cathode as well as anode in the test solution is shown in fig.5 and 6 for 1N hydrochloric acid with imidazole and 2-methyl imidazole at room temperature(303K). 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 and the cathodic and anodic Tafel slopes increased with increasing inhibitor concentration and the increase is predominant in the case of the former indicating that the cathodic inhibition is dominating through the inhibitive action is of mixed nature. The non-constancy of Tafel slopes for different inhibitor concentration reveals that the inhibitior act through their interference in the mechanism of the corrosion processes at the cathode as well as anode.

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

Reasons for inhibition

It has already been reported by many workers[37-39] that most of the organic inhibitors work by way of adsorption on the metal surface as has been established in the present work. Adsorption bond strength depends upon the electron density available at the point of adsorption. The point of adsorption may be any electron- donating element such as N, O, S, P , etc. present in the molecular structure of the inhibitor . If there are more than

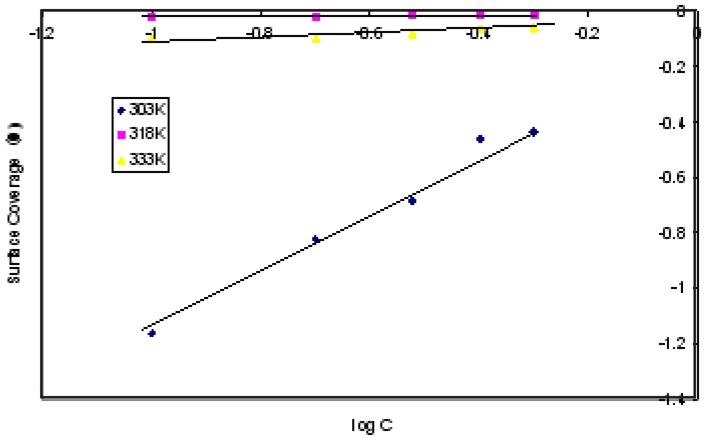

Fig. 4: Temkin's adsorption isotherm for corrosion behavior of mild steel in 1N hydrochloric acid with 2-methylimidazole

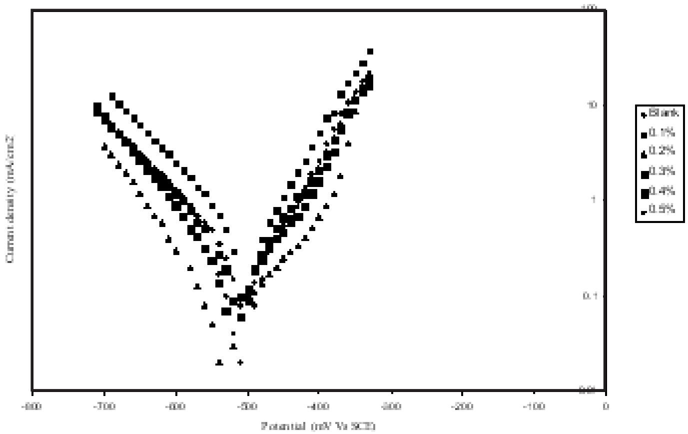

Fig. 5: Typical Potentiostatic curves for mild steel in 1N Hydrochloric acid with Imidazole

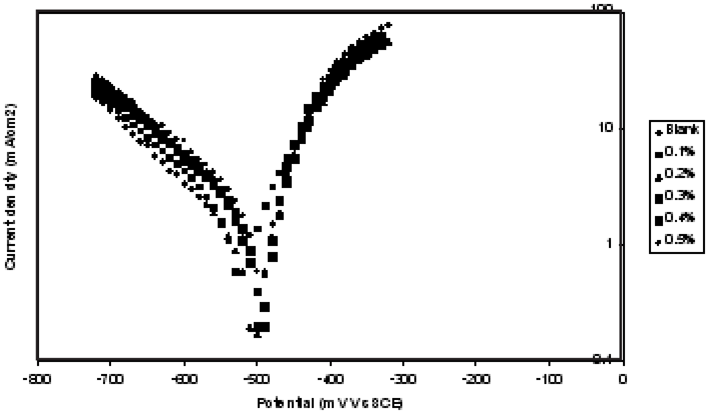

Fig. 6: Typical Potentiostatic curves for mild steel in 1N Hydrochloric acid with 2-methylimidazole

one electron donating elements present then which atom will have a higher tendency to become point of adsorption depends upon the distribution of electrons on the over all structure of the molecule. In the presence of an inhibitor, a thin black film has always been observed on the surface of the specimens. This shows that the inhibition is due to the formation of some complex film with the metal ions. The organic compounds used as inhibitors like Imidazole and 2-Methylimidazole have the following structure[40-41].

This inhibitors act as a proton acceptor in an acidic medium. It forms an organo metallic complex layer with the metal ions on surface of the metal, thus inhibiting corrosion. The N atoms act as the reaction centers in the complexation reaction with the metal ions. The adsorption of the inhibitors over mild steel surface may be through first N only which is supposed to be active center for adsorption of inhibitor molecule due to the presence of charge on it.

2 Methylimidazole shows the better inhibition than Imidazole. This is due to the structure of 2-Methlyimidazole; the substitution of the CH_3 group for H-at the second position in imidazole that improved the inhibitive effect[41].

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CONCLUSION

The following conclusions were made from the studies,

1. Corrosion rates of mild steel in 1N hydrochloric acid decreased with increasing concentration of Imidazole and 2-Methylimidazole.
2. The inhibition efficiency increased with respect to the concentration of inhibitors as it is assumed that the inhibition efficiency is equal to surface coverage.
3. The inhibition efficiency of Imidazole and 2-Methylimidazole in hydrochloric acid increased with rise in temperature up to 318K and then decreased.
4. The maximum inhibition efficiency of imidazole and 2-methylimidazole was found to be 96.68% and 97.51% respectively in 1N hydrochloric acid at 0.5% inhibitor concentration at 318K.
5. The adsorption of imidazole and 2-methylimidazole on mild steel surface from the acid solution follows Temkin's adsorption isotherm
6. The low and negative value of ΔG_{ads} indicated that the imidazole and 2-methyl- imidazole is physically adsorbed and spontaneous adsorption of inhibitors on the surface of mild steel.
7. The inhibition efficiency obtained from mass loss studies and polarization measurement shows fairly good agreement.
8. 2-Methylimidazole shows the better inhibition than Imidazole
9. It is found that the imidazole and 2-methylimidazole acting as mixed type inhibitor
10. Energy of activation (Ea) values indicates physical adsorption of the inhibitor on metal surface.

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