

The Effect of Imidazole and 2-Methyl Imidazole on the Corrosion of Mild Steel in Phosphoric Acid Solution

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Two azole compounds viz., Imidazole (IM) and 2-Methylimidazole (2-MIM) were studied to investigate their inhibiting action on corrosion of mild steel in phosphoric acid (H_3PO_4) solution by mass loss and polarization techniques at 302K-333K. It has been found that the inhibition efficiency of the all inhibitors increased with increase in inhibitor concentration and decreases with increasing temperature and also with increase in acid concentrations. The inhibition efficiency of these compounds showed very good inhibition efficiency. At 0.5% of IM and 2-MIM in 1N and 5N phosphoric acid solution at 302K to 333K for 5 hours immersion period, the inhibition efficiency of 2-Methylimidazole found to be higher than Imidazole. The adsorption of these compounds on the mild steel surface from the acids has been found to obey Tempkin's adsorption isotherm. The values of activation energy (E_a) and free energy of adsorption (ΔG_{ads}) were also calculated. The plots of $\log W_f$ against time (days) at 302K give straight line which suggested that it obeys first order kinetics and also calculate the rate constant k and half life time $t_{1/2}$. Surface was analyzed by SEM and FTIR spectroscopy.

Keywords : mild steel, phosphoric acid, corrosion inhibition, adsorption isotherm, potentiostatic polarization.

1. Introduction

Phosphoric acid is a major chemical product, which has many important uses, especially in the production of fertilizers. Most of the acid is produced from phosphate rock by wet process. Generally nickel-base alloys and stainless steel are frequently used in many parts of the wet process and a considerable quantity of data has been published about the resistance of these materials to corrosion by phosphoric acid solution.¹⁾⁻⁵⁾ Most of the previous studies were focused on the inhibition of stainless steel or chromium-nickel steel in HCl or H_2SO_4 solutions using organic compounds containing nitrogen, sulfur and oxygen atoms as corrosion inhibitors.⁶⁾⁻⁷⁾ Organic inhibitors are widely used in various industries. Among them, heterocyclic compounds comprise a potential class of inhibitors. There is wide consideration in the literature regarding corrosion inhibition studies by nitrogen containing heterocyclics.⁸⁾⁻¹⁵⁾ Heterocyclic compounds containing nitrogen and sulphur atoms are of particular importance as they often provide excellent inhibition compared with compounds containing only nitrogen or

sulphur.¹⁶⁾⁻²¹⁾ The corrosion inhibiting property of these compounds is attributed to their molecular structure. These compounds contain π electrons and heteroatoms, which induce greater adsorption of the inhibitor molecules onto the mild steel surface.

The aim of the present investigation was to examine the inhibitive action of Imidazole (IM) and 2-Methylimidazole (2-MIM) towards the corrosion of mild steel in 1N and 5N phosphoric acid by mass loss and potentiostatic polarization methods at 302K-333K.

2. Experimental

2.1 Mass loss measurement

Mild steel specimens were cut to the 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 previously.²²⁾⁻²⁴⁾ The surface of the specimens were polished with emery papers ranging from 110 to 410 grades and degreased with trichloroethylene. Specimens were dried and stored in vacuum desiccator containing silica gel. These specimens were

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initially weighed in an electronic balance. After that the specimens were suspended with the help of PTFE threads in conical flask containing 1N and 5N H₃PO₄ acid (in presence and in absence of inhibitors). The experiments were carried out at 302K, 313K and 333K. The specimens were removed after a definite exposure period, washed with water to remove any corrosion products and finally washed with acetone. After that they were dried in an oven and re-weighed. All the solutions were prepared using AR grade chemicals with double distilled water.

2.2 Potentiostatic polarization measurement

For potentiostatic measurements, mild steel electrode of 1 cm x 1cm dimensions with stem was cut. The stem and the face of the electrode were marked with araldite, so as to expose an area of 1 cm². The electrodes are polished using 1/0, 2/0, and 3/0 and 4/0 emery papers and degreased with trichloroethylene. Potentiostatic polarization measurements were carried out in three-electrode cell using BAS-100A model instrument. The potential of the test electrode was measured with respect to SCE and platinum was used as auxiliary electrode and the experiments were carried out at 302K to 333K.

3. Results and discussion

3.1 Mass loss studies

Table 1 and 2 show the values of inhibition efficiency (IE%), surface coverage (θ) and corrosion rate obtained for different concentrations of these inhibitors in 1N and 5N phosphoric acid (H₃PO₄) for immersion period of 5 hours at 302K-333K. From the mass loss value, the inhibition efficiency (IE%) and surface coverage (θ) were calculated using the following equation.²⁵⁾⁻²⁶⁾

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

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

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.

The mass loss study results clearly indicate the inhibition efficiency increase with increase in concentration of inhibitors and decrease with rise in temperature from 302K to 333K and with acid concentration from 1N to 5N. The values of corrosion rate and inhibition efficiencies of the inhibitor compounds were found to depend on their molecular structure. The inhibition efficiency of 2-Methy-

Table 1. Calculated corrosion rate, inhibition efficiency (IE%) and surface coverage (θ) values for Imidazole (IM) from mass loss data in 1N and 5N H₃PO₄.

Temp. (°K)	Conc. Of Imidazole (%)	1N			5N		
		Corrosion rate (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)	Corrosion rate (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)
302	Blank	6.80	-	-	26.22	-	-
	0.1	3.05	0.5520	55.20	15.68	0.4020	40.20
	0.2	2.40	0.6471	64.71	14.07	0.4632	46.32
	0.3	2.13	0.6879	68.79	11.48	0.5620	56.20
	0.4	1.76	0.7418	74.18	8.84	0.6627	66.27
	0.5	0.58	0.9146	91.46	5.64	0.7848	78.48
313	Blank	11.93	-	-	70.22	-	-
	0.1	5.95	0.5016	50.16	44.95	0.3598	35.98
	0.2	4.78	0.5992	59.92	42.69	0.3920	39.20
	0.3	4.46	0.6260	62.60	35.18	0.4990	49.90
	0.4	2.25	0.7280	72.80	28.32	0.5967	59.67
	0.5	1.09	0.9091	90.91	24.48	0.7314	73.14
333	Blank	19.82	-	-	157.39	-	-
	0.1	11.11	0.4396	43.96	127.85	0.1877	18.77
	0.2	9.09	0.5412	54.12	105.05	0.3316	33.16
	0.3	8.20	0.5862	58.62	89.37	0.4322	43.22
	0.4	6.71	0.6617	66.17	71.36	0.5466	54.66
	0.5	2.68	0.8650	86.50	51.30	0.6741	67.41

Table 2. Calculated corrosion rate, inhibition efficiency (IE%) and surface coverage (θ) values for 2-Methylimidazole (2-MIM) from mass loss data in 1N and 5N H₃PO₄.

Temp. (°K)	Conc. Of 2-MIm (%)	1N			5N		
		Corrosion rate (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)	Corrosion rate (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)
302	Blank	6.8	-	-	26.22	-	-
	0.1	2.67	0.6080	60.80	16.96	0.3530	35.30
	0.2	2.12	0.6879	68.79	13.04	0.5026	50.26
	0.3	1.92	0.7180	71.80	10.72	0.5910	59.10
	0.4	1.62	0.7620	76.20	7.58	0.7110	71.10
	0.5	0.48	0.9297	92.97	4.94	0.8115	81.15
313	Blank	11.93	-	-	70.22	-	-
	0.1	5.11	0.5720	57.20	49.04	0.3016	30.16
	0.2	4.09	0.6571	65.71	37.78	0.4620	46.20
	0.3	3.68	0.6912	69.12	30.26	0.5691	56.91
	0.4	3.08	0.7420	74.20	22.36	0.6816	68.16
	0.5	1.17	0.9020	90.20	14.21	0.7976	79.76
333	Blank	19.82	-	-	157.39	-	-
	0.1	10.07	0.4917	49.17	118.93	0.2444	24.44
	0.2	8.29	0.5817	58.17	96.04	0.3898	38.98
	0.3	7.05	0.6444	64.44	81.15	0.4844	48.44
	0.4	6.00	0.6975	69.79	60.57	0.6144	61.44
	0.5	3.15	0.8414	84.14	41.30	0.7376	73.76

imidazole found to be higher than Imidazole.

The activation energy *Ea* (KJ/mole), free energy of adsorption ΔG_{ads} (KJ/mole), rate constant *k* (sec⁻¹) and half-life *t*_{1/2}(sec) of corrosion of mild steel have been obtained by measuring the corrosion rate from the mass loss measurement in 1N and 5N phosphoric acid with and without inhibitors at 302K to 333K. Energy of activation (*Ea*) has been calculated from the slopes of plots of log *p* versus 1/*T* in Fig. 1 and 2 for Imidazole (IM) (similar plots were also obtained for 2-MIM) and also with the help of Arrhenius equation²⁷⁾⁻²⁹⁾

$$\log \frac{p_2}{p_1} = \frac{Ea}{2.303R} \left[-\frac{1}{T_1} - -\frac{1}{T_2} \right] \quad (3)$$

Where *p*₁ and *p*₂ are the corrosion rate at temperatures *T*₁ and *T*₂ respectively. The activation energy *Ea* are found to be 28.86 KJ/mole and 48.34 KJ/mole for 1N and 5N H₃PO₄ respectively. The *Ea* values for 1N and 5N H₃PO₄ containing inhibitors are found to be higher than that of without inhibitors. The higher values of *Ea* indicate physical adsorption of the inhibitors on metal surface³⁰⁾ and also indicate that besides, adsorption of these inhibitors are found to increase the activation energy of the corrosion process. The values of *Ea* calculated from the slopes of Arrhenius plot and by using equation-1 are approximately almost similar.

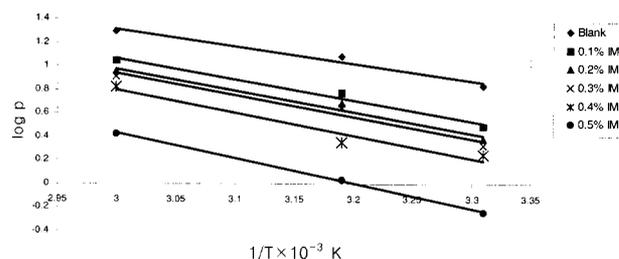


Fig. 1. Arrhenius plot for 1N H₃PO₄ with Imidazole

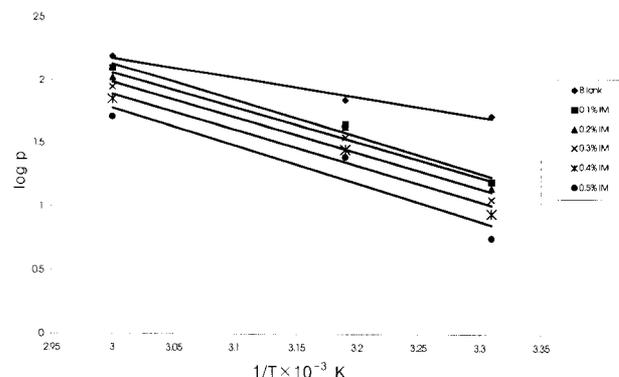


Fig. 2. Arrhenius plot for 5N H₃PO₄ with Imidazole

The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated from the following equation³¹⁾

Table 3. calculated values of activation energy Ea (KJ/mole), free energy of adsorption ΔGads (KJ/mole), rate constant k (Time⁻¹) and half-life t_{1/2} (time) for mild steel corrosion in 1N and 5N phosphoric acid with inhibitors.

Inhibitors	Conc. of Inhibitors (%)	Ea from Eqn.1 (KJ/mole)	Ea from Arrhenius plot (KJ/mole)	- ΔGads (KJ/mole)			Rate constant k x 10 ⁻⁶ (Sec ⁻¹)	Half -life t _{1/2} (Sec)
				302K	313K	333K		
IM + 1N H ₃ PO ₄	Blank	28.86	28.72	-	-	-	5.73	120934
	0.5	34.87	34.97	21.21	21.45	22.13	5.33	129997
	1.0	35.92	35.99	20.46	20.67	21.34	5.22	132641
	1.5	36.36	36.90	19.91	19.92	20.72	5.12	135406
	2.0	36.10	37.10	19.85	20.39	20.82	4.93	140521
	2.5	41.29	40.22	22.59	23.24	23.49	4.66	148573
2-MIM + 1N H ₃ PO ₄	Blank	28.86	28.72	-	-	-	5.73	120934
	0.5	35.81	36.02	22.25	22.68	23.23	5.22	132641
	1.0	36.79	36.70	21.40	21.81	22.32	5.06	136823
	1.5	35.09	36.90	20.74	21.16	21.93	4.96	139761
	2.0	35.32	37.02	20.59	21.06	21.80	4.77	145256
	2.5	50.75	49.50	23.59	23.51	23.49	4.45	155684
IM + 5N H ₃ PO ₄	Blank	48.34	48.74	-	-	-	22.82	30370
	0.5	56.61	56.10	19.68	19.94	18.75	21.48	32253
	1.0	56.23	56.70	18.57	18.49	18.94	20.84	33246
	1.5	55.36	56.90	18.55	18.57	19.01	20.55	33722
	2.0	56.34	57.10	18.89	18.85	19.48	19.46	35614
	2.5	59.56	59.10	19.89	19.85	20.36	18.74	36979
2-MIM + 5N H ₃ PO ₄	Blank	48.34	48.74	-	-	-	22.82	30370
	0.5	52.54	53.02	19.63	19.74	20.20	21.19	32702
	1.0	53.86	54.02	19.44	19.72	20.16	20.63	33592
	1.5	54.60	54.68	19.32	19.79	20.11	20.39	33981
	2.0	56.06	56.00	19.93	20.30	20.78	18.60	35908
	2.5	57.28	57.15	20.78	21.30	21.73	18.50	37463

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

and K is given by

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

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

The negative values of ΔGads given in Table 3 indicate the spontaneous adsorption of the inhibitor and are usually characteristics of strong interaction with the metal surface. It is found that the ΔGads values are less than (less - ve values) - 40 KJ/mole indicating that inhibitors are physically adsorbed on the metal surface.³²⁾⁻³³⁾

The values of rate constant k were evaluated from the plots of log W_f versus time days in Fig. 3 and 4 for Imidazole (IM). Similar plots were also obtained for 2-MIM. Linear plots were obtained which revealed first order kinetics. The values of half-life t_{1/2} were calculated using the equation below.²⁸⁾

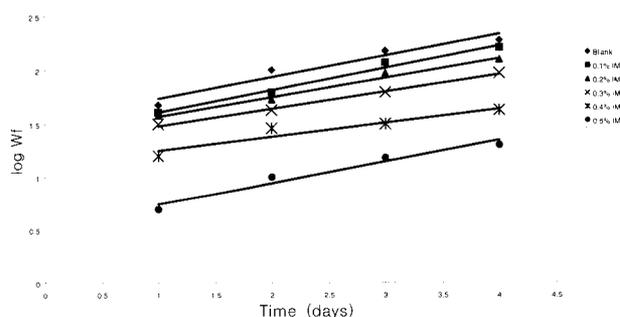


Fig. 3. Plot of log Wf versus time (days) for 1N H₃PO₄ with Imidazole

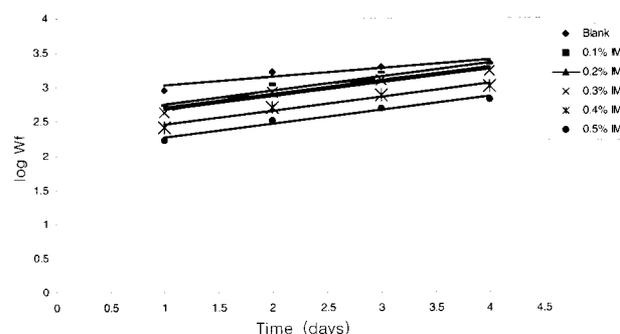


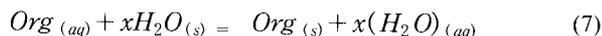
Fig. 4. Plot of log Wf versus time(days) for 5N H₃PO₄ with Imidazole

$$t_{1/2} = \frac{0.693}{k} \tag{6}$$

The rate constant k decreases with increase in concentration of inhibitors where as the half-life increases with concentration of inhibitors.²⁸⁾ The adsorption of the organic molecules can affect in several ways, the behaviour of the electrochemical reactions involved in the corrosion process. The action of organic inhibitors also depends on the type of interaction between the substance and the metallic surface. This interaction causes a change either in the electrochemical process mechanism or in the surface available to the process.⁴³⁾⁻⁴⁵⁾

3.2 Adsorption isotherms

The electrochemical process on the metal surface is likely to be closely related to the adsorption of the inhibitor³⁴⁾ and the adsorption is known to depend on the chemical structure of the inhibitor.³⁵⁾⁻³⁷⁾ The adsorption of the inhibitor molecules from aqueous solution can be regarded as quasubstitution process³⁵⁾ between the organic compound in the aqueous phase, $Org_{(aq)}$ and water molecules at the electrode surface, $H_2O_{(s)}$.



Where x the size ratio, is the number of water molecules displaced by one molecule of organic inhibitor.

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The most frequently used isotherms are those of Langmuir, Frumkin, Parsons, Temkin, Flory-huggins and Bockris-Sinkles.³⁸⁾⁻⁴¹⁾ All these isotherms are of the general form:

$$F(\theta, x) \exp(-a\theta) = KC \tag{8}$$

Where $f(\theta, x)$ is the configurational factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm.⁴²⁾

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 $\log C$ for different concentrations of the compound show a straight line indicating that the adsorption of the compounds from acids on mild steel surface follows Temkin's adsorption isotherm.³¹⁾ This also pointed to corrosion inhibition by these compounds being a result of their adsorption on the metal surface. Fig 5 and 6 shows the Temkin's adsorption isotherm for Imidazole (IM) in 1N

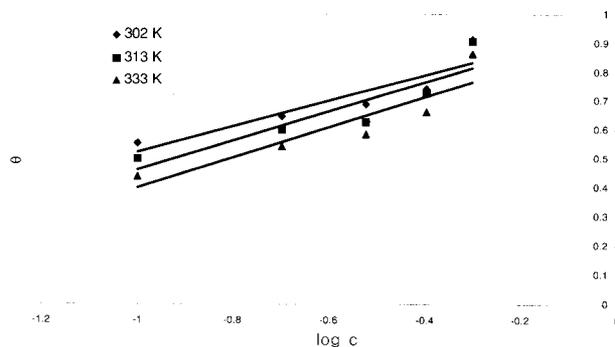


Fig. 5. Temkin's adsorption isotherm plot for 1N H₃PO₄ with Imidazole

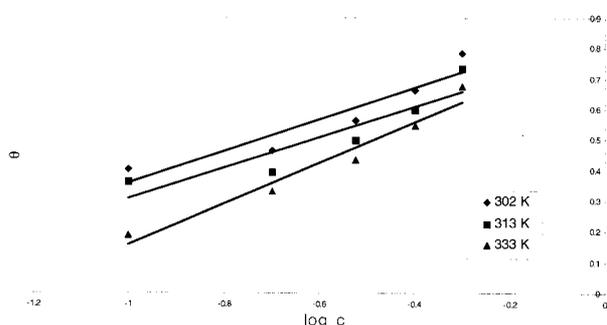


Fig. 6. Temkin's adsorption isotherm plot for 5N H₃PO₄ with Imidazole

and 5N H₃PO₄. Similar plots were also obtained for 2-MIM.

3.2.1 Potentiostatic polarization studies

The polarization measurements were carried out potentiostatically using BAS-100A model instrument. The measurements of corrosion current by polarization method for mild steel in 1N and 5N H₃PO₄ containing various concentration of IM and 2-MIM were studied. The polarization behaviour of mild steel functioning as cathode as well as anode in the test solutions is shown in Fig.7 for 1N H₃PO₄ at 302K for Imidazole (IM). Similar curves were also obtained for 2-MIM in 1N and 5N phosphoric acid at 302K to 333K and the electrochemical data obtained from the studies are shown in Table 4. It is evident that azoles bring about considerable polarization of the cathode as well as anode. It was, therefore, inferred that the inhibitive action is of mixed type. The cathodic and anodic Tafel slopes increased with increasing inhibitor concentrations and the increase was predominant in the case of the former indicating that the cathodic inhibition was dominating through the inhibitive active is of mixed nature. The non-constancy of Tafel slopes for different inhibitor concentration reveals that the inhibitor act

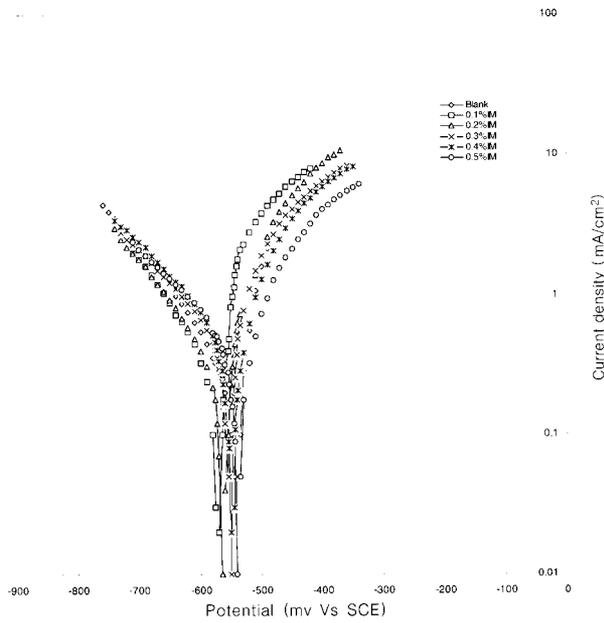


Fig. 7. Typical potentiodynamic curves for mild steel in 1N H₃PO₄ with Imidazole at 302k

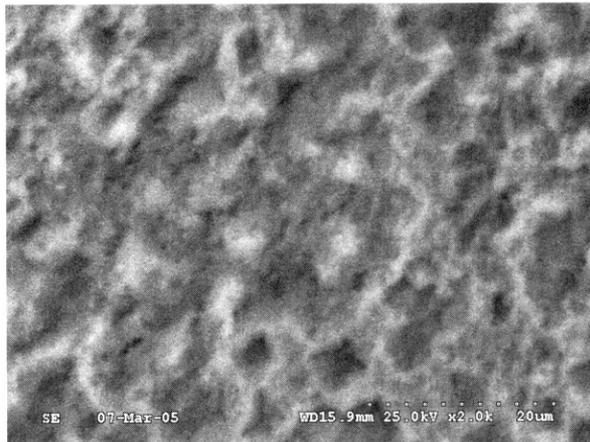


Fig. 8. SEM FOR MILD STEEL IN 5N H₃PO₄

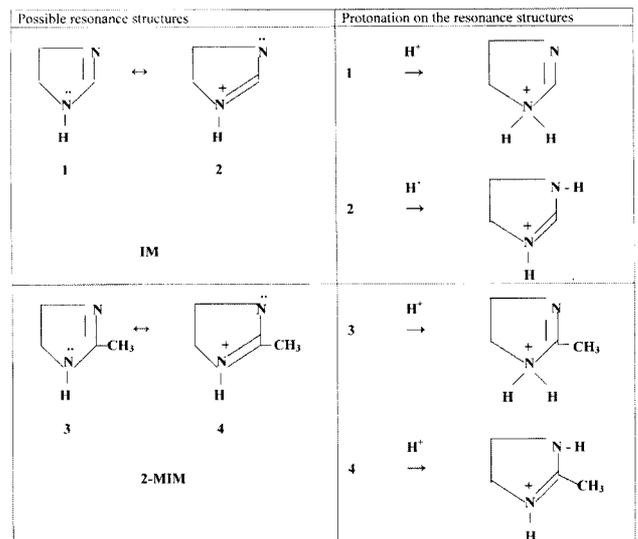
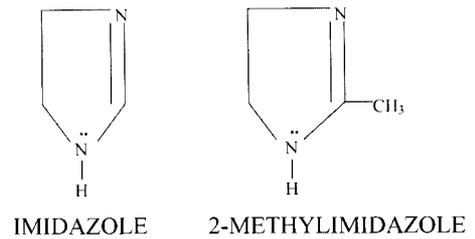
through their interference in the mechanism of the corrosion processes at the cathode as well as the anode.

The corrosion parameters deduced from Tafel polarization such as corrosion current i_{corr} , corrosion potential E_{corr} , Tafel slopes b_a and $-b_c$ and inhibition efficiency are given in Table 4. The i_{corr} values were decreased with the increasing concentration of inhibitors. The inhibition efficiencies were determined from the values of corrosion current and the inhibition efficiency values were found to show good agreement, with those obtained from mass loss measurements.

3.3 Reasons for inhibition

1. It has already been reported by many workers⁴⁶⁾⁻⁴⁹⁾ 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. Point of adsorption may be any electron-donating element such as N, O, S, P, Se, etc. present in the molecular structure of the inhibitor. If there are more than 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 overall structure of the inhibitor 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.⁵⁰⁾⁻⁵¹⁾



This inhibitors act as a proton acceptor in an acidic medium. It forms an organometallic complex layer with the metal ions on surface of the metal, thus inhibiting corrosion. The N atoms act as the reaction centers in the

Table 4. Electrochemical polarization parameters for the corrosion behaviour of mild steel in 1N and 5N Phosphoric acid in absence and presence of inhibitors at 302K-333K.

Conc. Of inhibitors (%)	1N					5N				
	E _{corr} Vs SCE(mv)	I _{corr} μ A/cm ²	Tafel Constants (mv/decade)		IE%	E _{corr} Vs SCE(mv)	I _{corr} μ A/cm ²	Tafel Constants (mv/decade)		IE%
			ba	-bc				ba	-bc	
302K										
Blank	-543	210	50	130	-	-510	700	50	150	-
0.1 IM	-573	98	50	129	53.33	-538	427	48	149	39.00
0.2 IM	-563	76	48	124	63.38	-535	388	48	146	44.57
0.3 IM	-553	64	46	120	69.52	-523	314	46	144	55.14
0.4 IM	-548	56	49	117	73.33	-518	247	44	142	64.71
0.5 IM	-539	22	45	120	89.52	-515	160	40	140	77.14
Blank	-543	210	50	130	-	-510	700	50	150	-
0.1 2MIM	-565	86	50	128	59.00	-530	415	49	146	40.71
0.2 2MIM	-563	70	45	126	66.67	-528	362	48	144	48.29
0.3 2MIM	-558	64	47	120	69.52	-520	303	44	140	56.71
0.4 2MIM	-554	54	48	116	74.29	-519	215	43	137	69.29
0.5 2MIM	-548	19	40	110	90.95	-517	134	39	134	80.86
313K										
Blank	-535	680	100	150	-	-505	1000	30	175	-
0.1 IM	-550	347	95	149	48.97	-520	669	28	173	33.10
0.2 IM	-546	297	93	147	56.36	-516	629	28	174	37.10
0.3 IM	-542	268	92	143	60.59	-513	528	27	172	47.20
0.4 IM	-540	199	87	140	70.74	-510	429	26	170	57.10
0.5 IM	-539	68	85	138	90.00	-508	293	25	165	70.70
Blank	-535	680	100	150	-	-505	1000	30	175	-
0.1 2MIM	-545	293	95	146	56.91	-516	643	27	172	35.70
0.2 2MIM	-542	240	94	144	64.71	-515	538	25	170	46.20
0.3 2MIM	-541	215	90	140	68.38	-511	448	24	169	55.20
0.4 2MIM	-538	176	86	136	74.12	-508	320	23	166	68.00
0.5 2MIM	-537	75	83	130	88.97	-507	209	23	164	79.10
333K										
Blank	-523	1400	150	150	-	-483	3000	75	190	-
0.1 IM	-538	795	140	149	43.21	-500	2467	73	189	17.77
0.2 IM	-536	657	141	146	53.07	-497	2041	70	184	31.97
0.3 IM	-535	600	138	144	57.14	-492	1732	68	183	42.27
0.4 IM	-530	490	136	141	65.00	-488	1394	67	184	53.53
0.5 IM	-528	203	130	138	85.50	-486	956	65	180	68.13
Blank	-523	1400	150	150	-	-483	3000	75	190	-
0.1 2MIM	-535	714	140	148	49.00	-496	2276	71	186	24.13
0.2 2MIM	-533	588	135	140	58.00	-493	1891	70	184	36.97
0.3 2MIM	-531	506	133	135	63.86	-491	1548	68	180	48.40
0.4 2MIM	-530	448	130	130	68.00	-487	1174	65	176	60.87
0.5 2MIM	-527	235	128	132	83.21	-586	776	62	173	74.13

complexation reaction with the metal ions.⁵¹⁾ The adsorption of the inhibitors over mild steel surface may be through first nitrogen only which is supposed to be active center for adsorption of inhibitor molecule due to the presence of charge on it.

2. 2-Methylimidazole shows the better inhibition than Imidazole. This is due to the structure of 2-Methylimidazole; the substitution of the CH₃ group for H-at the second position improved the inhibitive effect.⁵¹⁾

3.4 Scanning electron microscopy

Surface of polished mild steel specimen immersed in 5N H₃PO₄ in the presence of inhibitors (IM and 2-MIM) were examined using scanning electron microscope (SEM).

Fig. 9 and 10 shows the surface photograph of mild steel specimens immersed 5N H₃PO₄ with inhibitors. In the case of blank, the corroded metal surface with etched

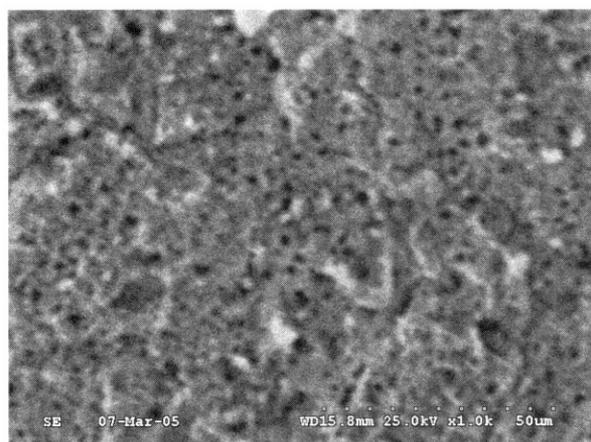


Fig. 9. SEM for mild steel in 5N H₃PO₄ with IM

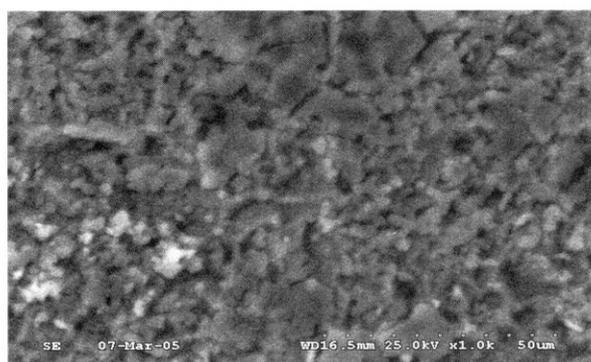


Fig. 10. SEM for mild steel in 5N H₃PO₄ with 2-MIM

grain boundaries and corrosion products are clearly seen in Fig 8. But in the presence of inhibitors there is formation of adsorbed layer of inhibitors on the metal surface without any corrosion products as seen in Fig.9 and 10

3.5 FTIR spectroscopy

3.5.1 Imidazole (IM)

Fig. 11 shows the FTIR spectra for corrosion of mild steel in 5N H₃PO₄ with IM. Heteroaromatic containing an N-H group shows N-H stretching absorption in region of 3634 cm⁻¹. Ring stretching vibrations occur in the general region at 1645 cm⁻¹ and C=N stretching appears at 1645 cm⁻¹. The absorption involves stretching and contraction of all of the bonds in the ring and interaction between these stretching modes. In the phosphoric acid medium P=O stretching (aromatic) appears at 1142 cm⁻¹ and PH₂ bend scissoring appears at 1049 cm⁻¹. Out of plane NH wagging is responsible for a broad band of medium intensity in the 652 cm⁻¹. So it is suggested that IM is

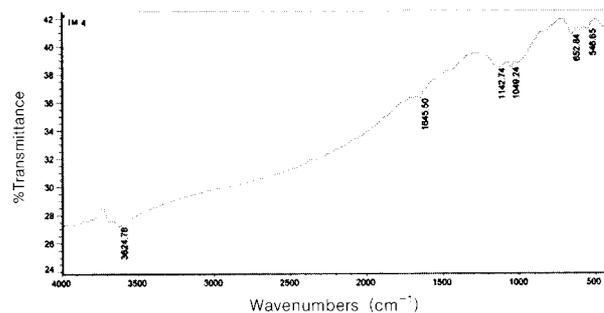


Fig. 11. FTIR for mild steel in 5N H₃PO₄ with IM

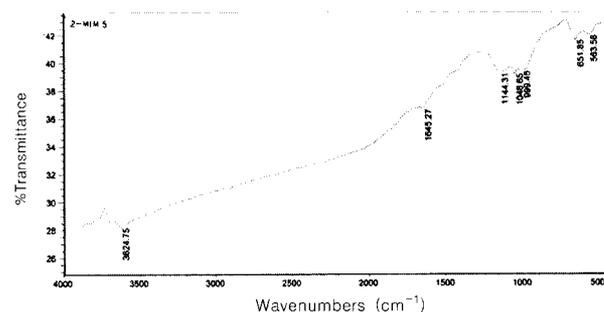


Fig. 12. FTIR for mild steel in 5N H₃PO₄ with 2-MIM

coordinated to Fe²⁺ resulting in the formation of Fe²⁺-IM complex on the metal surface.

3.5.2 2-Methylamine (2-MIM)

Fig. 12 shows the FTIR spectra for corrosion of mild steel in 5N H₃PO₄ with 2-MIM. Heteroaromatic containing an N-H group shows N-H stretching absorption in the region of 3624 cm⁻¹. Ring stretching vibrations occur in the general region at 1645 cm⁻¹ and C=N stretching appears at 1645 cm⁻¹. The absorption involves stretching and contraction of all of the bonds in the ring and interaction between these stretching modes. In the phosphoric acid medium P=O stretching (aromatic) appears at 1144 cm⁻¹ and PH₂ bend scissoring appears at 1048 cm⁻¹. Out-of plane N-H wagging is responsible for a broad band of medium intensity in the 651 cm⁻¹. The number of adjacent hydrogen atoms bending in phase determines the C-H out-of-plane bending absorption pattern of the heteroaromatics. The C-H out-of-plane and ring bending absorption of the alkylimiazole appear at 999 cm⁻¹. So it is suggested that 2-MIM is coordinated to Fe²⁺ resulting in the formation of Fe²⁺-2-MIM complex on the metal surface.

4. Conclusion

- 1) All the azoles acted as efficient corrosion inhibitors in 1N and 5N phosphoric acid
- 2) The effect of temperature on the corrosion behaviour

of mild steel indicated that inhibition of inhibitors decreased with increasing temperature.

3) The inhibition efficiency decreased with increasing concentration of phosphoric acid.

4) The inhibition efficiency value obtained from mass loss studies and polarization measurements showed fairly good agreement. The corrosion inhibition appears to be of mixed type.

5) The two azoles inhibited corrosion by adsorption mechanism and the adsorption of these compounds from acid solution followed Temkin's adsorption isotherms at all the concentrations.

6) From the values of activation energy E_a , the inhibition was probably due to the adsorption of inhibitors on the metal surface.

7) The ΔG_{ads} values were negative which suggest that they were strongly adsorbed on the metal surface. The negative values of ΔG_{ads} indicated the spontaneous adsorption of the inhibitors and were usually characteristic of strong adsorption with the metal surface.

8) In the kinetic studies, linear plots were obtained which revealed first order kinetics.

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References

1. A. C. Hart, *Br Corros. J.*, **6**, 205 (1971).
2. A. C. Hart, *Br Corros. J.*, **8**, 66 (1973).
3. R. M. Saleh, M. M. Badran, A. A. Alhosary, and H. A. El Dahan, *Br Corros. J.*, **3**, 105 (1988).
4. P. Barrco, G. Chairò and A. C. Farina, *Proc. of the 11th International Corrosion Congress, Florence and Italy*, vol **2**, 2.539 (1990).
5. F. Smith and N. H. Van Droffelaar, *Br. Corros. J.*, **26**, 265 (1991).
6. A. M. Al-Mayout, A. A. Al-Suhybani, and A. K. Al-Ameer, *Desalination* **116**, 25 (1998) and references therein.
7. S. Bilgic and N. Caliskan, *J. Appl. Electrochem.*, **31**, 79 (2001) and references therein.
8. S. L. Granese, B. M. Rosales, C. Oviedo, and J. O. Zerbino, *Corros. Sci.*, **33**, 1439 (1992).
9. G. Subramaniam, K. Balasubramaniam, and P. Shridhar, *Corros. Sci.*, **30**, 1019 (1990).
10. S. N. Banerjee and S. Mishra, *Corrosion*, **45**, 780 (1989).
11. S. Hettiarachchi, Y. W. Chain, R. B. Wilson Jr, and V. S. Agarwala, *Corrosion*, **45**, 30 (1989).
12. C. R. Anderson and G. M. Schmid, *Corros. Sci.*, **24**, 325 (1984).
13. E. Stupnisek-lisac, M. Metikos-Hukovic, D. Lencic, J. Vorkapic-Furac, and K. Borkovic, *Corrosion*, **48**, 924 (1992).
14. E. Stupnisek-Lisac, K. Berkovic, and J. Vorakapic-Furac, *Corros. Sci.*, **12**, 1189 (1988).
15. S. N. Raicheva, B. V. Aleksiev, and E. J. Sokolov, *Corros. Sci.*, **3**, 343 (1993).
16. M. Ajmal, A. S. Mideen, and M. A. Quraishi, *Corros. Sci.*, **36**, 78 (1994).
17. M. A. Quraishi, M. A. W. Khan, M. Ajmal, and S. Muralidharan, *Portg. Electrochem. Acta*, **13**, (1995).
18. M. A. Quraishi, M. A. W. Khan, M. Ajmal, S. Muralidharan, and S. V. Iyer, *Anticorros methods Mater*, **43**, 5 (1996).
19. M. A. Quraishi, M. A. W. Khan, M. Ajmal, S. Muralidharan, and S. V. Iyer, *J. Appl. Electrochem.*, **26**, 1253 (1996).
20. M. A. Quraishi, M. A. W. Khan, M. Ajmal, S. Muralidharan, and S. V. Iyer, *Br. Corros. J.*, **32**, 72 (1997).
21. M. A. Quraishi, M. A. W. Khan, M. Ajmal, S. Muralidharan, and S. V. Iyer, *Corrosion*, **53**, 475 (1997).
22. P. M. Mathur and T. Vasudavan, *Corrosion*, **38**, 17 (1982).
23. ASTM G 31-72, "Standard practice for Laboratory Immersion Corrosion testing of metals", West Conshohocken, PA; ASTM, (1990).
24. M. Ajmal, A. S. Mideen, and M. A. Quraishi, *Corros. Sci.*, **36**, 79 (1994).
25. I. D. Talati and R. M. Modi, *Trans. SAEST*, **11**, 259 (1986).
26. L. A. Al-Shamma, J. M. Saleh, and N. A. Hikmat, *Corros. Sci.*, **27**, 221 (1987).
27. N. Subramanian and K. Ramakrishnaiah, *Ind. J. Tech.*, **8**, 369 (1970).
28. E. E. EBENSO, *Bull. Electrochem.*, **19**(5), 209 (2003).
29. P. C. Okafor, E. E. Ebenso, U. J. Ibok, U. J. Ekpe, and M. I. Ikpi, *Trans. SAEST*, **38**, 91 (2003).
30. I. N. Putilova, V. P. Barannik, and S. S. Balezin, *Metallic Corrosion Inhibitors*, p.30, Pergamon Press, Oxford, 1960.
31. M. A. Quraishi and R. Sardar, *Bull Electrochem.*, **18**(11) 515 (2002).
32. S. Brinic, A. Grubac, R. Babic, and M. Metikos-Hukovic, *8th Eur Symp Corros. Inhib.*, **1**, 197 (1995).
33. G. K. Gomma and M. H. Wahdan, *Ind. J. Chem. Technol.*, **2**, 107 (1995).
34. N. Hackerman, *Corrosion*, **18**, 332t (1962).
35. B. G. Atya, B. E. El-Anadouli, and F. M. El-Nizamy, *Corros. Sci.*, **24**, 497 (1984).
36. X. L. Cheng, H. Y. Ma, S. H. Chen, R. Yu, X. Chen, and Z. M. Yao, *Corros. Sci.*, **41**, 321 (1999).
37. M. Bouayed, H. Rabaa, A. Srhiri, J. Y. Saillard, A. Ben Bachir, and L. A. Beuze, *Corros. Sci.*, **41**, 501 (1999).
38. A. N. Frumkin, *Z. Phys. Chem.*, **116**, 446 (1925).
39. O. Ikeda, H. Jimbo, and H. Jaumura, *J. Electroanal. Chem.*, **137**, 127 (1982).
40. R. Parsons, *J. Electroanal. Chem.*, **7**, 136 (1964).
41. J. O. M. Bockris and D. A. J. Swinkels, *J. Electrochem.*

- Soc.*, **111**, 736 (1964).
42. B. Ateya, B. El-Anadouli, F. El-Nizamy, *Corros. Sci.*, **24**, 509 (1984).
43. S. L. Granese, *Corros. Sci.*, **44**(6), 322 (1988).
44. B. B. Damaskin, Adsorption of organic compounds on electrodes, p.221 Plenum Press New York, 1971.
45. S. M. Mayanna, *J. Electrochem. Soc.*, **122**, 251 (1975).
46. N. Hackerman and R. M Hurd, *1st International Congress, Metallic Corrosion*, p.166 Butterworths, London, 1962.
47. R. J. Meakins, *J. Appl. Electrochem.*, **13**, 339 (1963).
48. R. J. Meakins, *Brit. Corros. J.*, **6**, 111 (1971).
49. P. Sharma and J. N. Gaur, *J. Electrochem. Soc. India*, **25**, 4 (1976).
50. R Walker, *Corrosion*, **32**(10), 414 (1976).
51. S. N. Raicheva, B. V. Aleksiev, and E. I. Sokolova, *Corros. Sci.*, **34**(2), 351 (1993).