

An Investigation on the Tetrahydropyrimidine Derivatives as Acid Corrosion Inhibitors for Mild Steel

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The corrosive behavior of mild steel in 0.05 M to 10 M H₂SO₄ solutions containing different concentrations of tetrahydropyrimidine derivatives (THPM) was investigated using weight loss method, gasometric technique, electrochemical studies which include AC - impedance and potentiodynamic polarization method, atomic absorption studies and synergistic effect. The results obtained reveal that THPM derivatives is an efficient mixed type inhibitor but slightly anodic and it is more effective in reducing corrosion of mild steel in H₂SO₄ media. The adsorption of the inhibitor on the mild steel surface obeys the Langmuir adsorption isotherm. The thermodynamic parameters of adsorption reveal a strong interaction and spontaneous adsorption of THPM on the mild steel surface. The influence of temperature and inhibitor concentration on the corrosion of mild steel has also been investigated.

Keywords : mild steel, corrosion inhibitor, THPM

1. Introduction

Sulphuric acid solutions have been used for some treatments of metallic materials. Inhibiting action of several families of organic compounds were reported in literature. Inhibitors should be added in order to prevent corrosion and acid consumption during these treatments. Mild steel has found extensive application in various industries. It undergoes corrosion, but to a greater extent in acidic environment. Acidic solutions are used extensively in chemical and several industrial processes such as acid pickling, acid cleaning, acid descaling and oil wet cleaning, etc..¹⁾ Chemical inhibitors are often used for these processes mainly to control the metal dissolution and acid consumption. Most well-known acid inhibitors are organic compounds containing nitrogen, sulfur, and oxygen atoms. Among them, nitrogen-containing heterocyclic compounds are considered to be effective corrosion inhibitors on steel in acid media.²⁾ N-heterocyclic compound inhibitors act by adsorption on the metal surface, and the adsorption of N-heterocyclic inhibitor takes place through nitrogen heteroatom, as well as those with triple or conjugated double bonds or aromatic rings in their molecular structures.

Up to now, many N-heterocyclic compounds, such as imidazoline derivatives,³⁾ 1,2,3-triazole derivatives,⁴⁾ 1,2,4-triazole derivatives,^{2),5)-9)} tetrazole derivatives,^{10),11)} pyr-

role,¹²⁾ pyridine derivatives,¹³⁾⁻¹⁵⁾ pyrazole derivatives,¹⁶⁾⁻¹⁹⁾ bipyrazole derivatives,^{20),21)} pyrimidine derivatives,²²⁾ pyridazine derivatives,²³⁾ indole derivatives,²⁴⁾⁻²⁶⁾ benzimidazole derivatives,²⁷⁾⁻³¹⁾ and quinoline derivatives³²⁾ have been used for the corrosion inhibition of iron or steel in acidic media. These organic inhibitors decrease corrosion current density by adsorption to the metal surface. Inhibitor adsorption is influenced by factors such as the nature and surface charge on the metal and the type of aggressive media, the structure of the inhibitor, and the nature of its interaction with the metal surface.

Synergistic inhibition is an effective means to improve the inhibitive force of inhibitor, to decrease the amount of usage and to diversify the application of inhibitor in acidic media. It is necessary for corrosion scientists to discover, explore and use synergism in the complicated corrosive media. Actually, many investigations concerning synergistic inhibition have been carried out and are being carried out. Feng et al.³³⁾ have studied the synergistic inhibition between propyl alcohol and iodide ion for steel corrosion in sulphuric acid. Zhang et al.³⁴⁾ have investigated synergistic effect of 2-mercapto benzimidazole and KI on copper corrosion inhibition in sulphuric acid. Tang et al.³⁵⁾ have supposed that for the corrosion inhibition of steel in hydrochloric acid, there is a synergism between chloride ion and neutral red, and the synergism between them played an important role in the process of adsorption.

The aim of the present study was to investigate the in-

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hibition efficiency of tetrahydropyrimidine derivatives in 0.05 M to 10 M H₂SO₄ solutions using chemical and electrochemical methods. Meanwhile, synergism has become an increasingly important phenomenon and serves as the basis for most modern corrosion inhibiting formulations. So the synergistic effect was studied by the addition of 1 mM KI, 1 mM KCl, 1 mM KBr, 1 mM ZnSO₄, 1 mM NiSO₄ and 1 mM MgSO₄ has also been studied in order to ascertain the specific mode in which the compound exerts its inhibiting action.

2. Experimental

Mild steel specimen of composition (wt %), carbon (0.084), manganese (0.369), silicon (0.129), phosphorous (0.025), sulphur (0.027), chromium (0.022), molybdenum (0.011), nickel (0.013), iron (rest %) has been taken for the present investigation. The mild steel specimen of size 5 cm × 2 cm × 0.05 cm were pickled with concentrated HCl, washed, dried and polished using emery sheets of 1/0, 2/0, 3/0 and 4/0 grades. The mild steel rod of same composition embedded in Teflon with an exposed surface of 0.785 cm² was used for electrochemical methods. Tetrahydropyrimidine derivatives were synthesized by following the reported procedure. It is a cyclo condensation reaction of ethylacetoacetate with aldehyde and urea.³⁶ It is carried out by simple heating the mixture of three compounds dissolved in ethanol with catalytic amount of HCl at reflux condition. i.e., A mixture of aldehydes (3.0 mole) ethylacetoacetate (4.2 ml), urea (2 mole)/thiourea (3.8 mmole) and fused CaCl₂ (0.3 mole) was taken in an open conical flask and was irradiated inside a microwave oven at medium power (450 W) for a total of 2.0 min, after completion, the reaction mixture was cooled and poured into ice and stirred for sometime. The product precipitated out as solid, which was filtered and recrystallised from ethanol. The concentration range of the inhibitors employed was 0.5 to 10.

The specimens were suspended into the solutions. Care was taken to ensure complete immersion. After three hours specimens were removed, washed with running water, dried and weighed and weight loss was calculated. A blank was carried out without inhibitors. The effects of temperature were known by carrying out the same procedure at different temperature range i.e., 40 °C, 50 °C and 60 °C using thermostat. Gasometric techniques were also employed.³⁷ The specimens were suspended from the hook into the cell containing 200 ml of 1 M H₂SO₄. The temperature was maintained at about 30 ± 1 °C and was maintained constant. Gasometric measurements were made for a period of an hour and simultaneously a duplicate was con-

ducted. Electrochemical studies were performed using platinum electrode and a saturated calomel electrode. Electrochemical impedance spectroscopy (EIS) and Tafel polarization were conducted in an electrochemical measurement unit. The EIS measurements were made at corrosion potentials over a frequency range of 10 kHz to 0.01 Hz with signals amplitude of 10 mV. The Tafel polarization measurements were made after EIS for a potential range of -200 mV to +200 mV with respect to open circuit potential, at a scan rate of 1 mV/sec. The I_{corr}, E_{corr}, R_t and C_{dl} values were obtained from the data using the corresponding "corr view" and "z view" software's.

Atomic absorption spectrophotometer was used for estimating the amount of dissolved iron in the corrodent solution containing various concentrations of the inhibitors in 1 M H₂SO₄ after exposing the mild steel specimen for three hours. The synergistic effect was studied by the addition of 1 mM KI to the mild steel specimen immersed in 1 M H₂SO₄ containing various concentrations of the inhibitors for a duration of three hours. The same procedure was repeated by the addition of 1 mM KCl, 1 mM KBr, 1 mM ZnSO₄, 1 mM NiSO₄, 1 mM MgSO₄.

3. Results and discussion

The structure, yield and melting point of tetrahydropyrimidine derivatives are shown in Table 1. The inhibition efficiency of THPM derivatives by weight loss method is shown below in Table 2. From the data it is evident that the inhibition efficiency of the compounds increases with increase in inhibition concentration as shown on Fig. 1. The surface coverage (θ) for different concentrations of the inhibitor were calculated. A plot of C/θ Vs concentration gives a straight line confirming that the absorption of these compounds on mild steel surface obeys Langmuir adsorption isotherm (Fig. 2). The logarithm of the corrosion rate of mild steel is represented as a straight line function of $1000/T$ where T is the temperature in Kelvin (Fig. 3). Using the Arrhenius plots, the free energy of adsorption ΔG°_{ads} and activation energy E_a were calculated (Table 3). The weight loss data obtained at high temperature were calculated and are presented in Table 4. The data clearly revealed that inhibition efficiency decreases with increase in temperature.

Table 5 gives the value of inhibition efficiency obtained using gasometric method and atomic absorption spectrophotometric study. The gasometric method reveals that the volume of gas collected decreased with the addition of inhibitors causing the inhibition efficiency to increase with the increase in the concentration of the inhibitor. There is a good agreement between the values of inhibition

Table 1. Physical characterization of the inhibitors

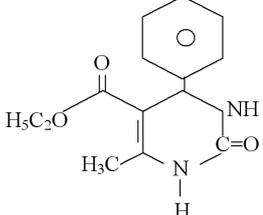
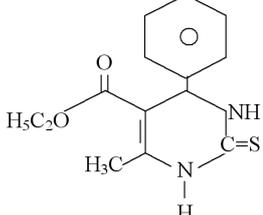
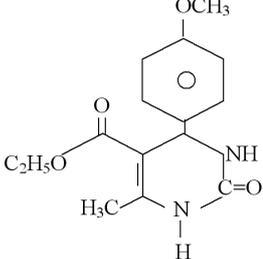
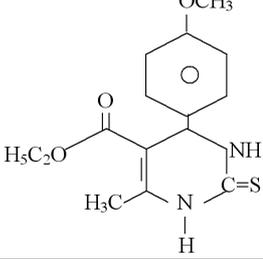
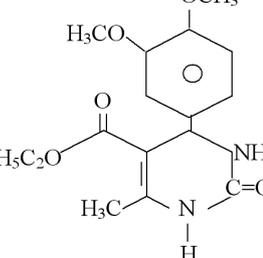
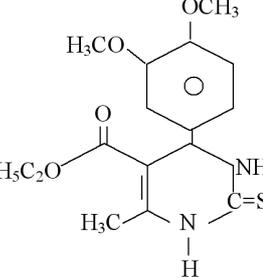
S. No.	Structure of the compounds	Colour	Yield (%)	Melting point
1	 <p>ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate THPM 1</p>	Dark Yellow	92	100
2	 <p>ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate THPM 2</p>	Yellow	95	98
3	 <p>ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate THPM 3</p>	Yellow	85	95
4	 <p>ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate THPM 4</p>	Pale Yellow	90	115
5	 <p>ethyl 4-[4(dimethoxymethyl)phenyl]-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate THPM 5</p>	Green	87	127
6	 <p>ethyl 4-[4(dimethoxymethyl)phenyl]-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate THPM 6</p>	Light Green	91	132

Table 2. Inhibition efficiencies of various concentrations of the inhibitors for mild steel corrosion in 1 M H₂SO₄ obtained by weight loss measurements at 30±1 °C

Name of the inhibitor	Concentration (mM)	Weight loss (g)	Inhibition efficiency (%)	Degree of surface coverage (θ)	Corrosion rate (mpy)
THPM 1	Blank	0.4849	-	-	7401.78
	0.5	0.0909	81.2	0.81	1387.55
	2.5	0.0610	87.4	0.87	931.14
	5.0	0.0458	90.6	0.91	699.12
	7.5	0.036	92.6	0.93	549.52
	10.0	0.0336	93.1	0.93	512.89
THPM 2	Blank	0.5378	-	-	8209.28
	0.5	0.124	76.9	0.77	1892.81
	2.5	0.0809	84.9	0.85	1234.90
	5.0	0.062	88.5	0.88	946.44
	7.5	0.056	89.6	0.90	854.81
	10.0	0.0249	95.4	0.95	940.00
THPM 3	Blank	0.4849	-	-	7401.78
	0.5	0.0743	84.7	0.85	1134.16
	2.5	0.0511	89.5	0.89	780.02
	5.0	0.0303	92.6	0.93	547.99
	7.5	0.0303	93.8	0.94	462.52
	10.0	0.0222	95.4	0.95	338.87
THPM 4	Blank	0.5378	-	-	8209.28
	0.5	0.063	88.3	0.88	961.67
	2.5	0.041	92.4	0.92	625.84
	5.0	0.0218	95.9	0.96	332.77
	7.5	0.026	96.2	0.96	314.45
	10.0	0.0152	97.2	0.97	232.02
THPM 5	Blank	0.4849	-	-	7401.78
	0.5	0.0432	91.1	0.91	659.43
	2.5	0.0187	96.1	0.96	285.45
	5.0	0.0126	97.4	0.97	192.33
	7.5	0.0096	97.9	0.98	146.54
	10.0	0.0088	98.2	0.98	134.33
THPM 6	Blank	0.2950	-	-	4503.04
	0.5	0.032	89.2	0.89	312.92
	2.5	0.0169	94.3	0.94	257.97
	5.0	0.0134	95.4	0.95	204.55
	7.5	0.0077	97.4	0.97	117.54
	10.0	0.0021	99.3	0.99	32.06

Table 3. Activation energies(E_a) and free energy of adsorption(ΔG^o_{ads}) for the corrosion of mild steel in 1 M H₂SO₄ at 10 mM concentration of the inhibitors

Name of the inhibitor	E _a (kJ)	ΔG ^o _{ads} at various temperatures (kJ)			
		303 K	313 K	323 K	333 K
Blank	82.92	-	-	-	-
THPM 1	86.74	-10.86	-9.04	-9.11	-9.04
THPM 2	88.14	-11.04	-10.91	-10.90	-10.73
THPM 3	92.36	-11.37	-11.38	-11.02	-10.67
THPM 4	106.14	-13.77	-12.64	-11.31	-11.20
THPM 5	101.38	-13.72	-12.32	-11.23	-11.01
THPM 6	105.34	-17.41	-14.03	-9.93	-9.76

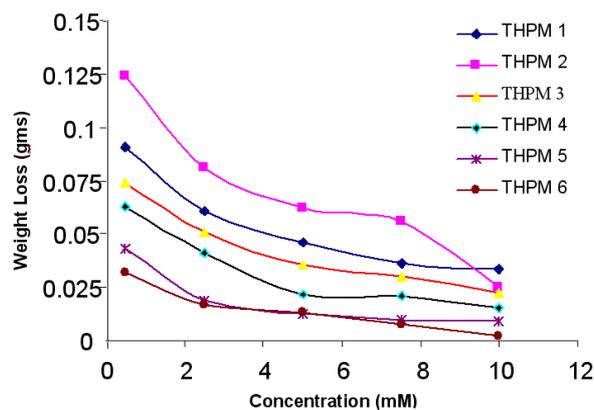


Fig. 1. Plot of weight loss vs concentration of inhibitors

Table 4. Inhibition efficiencies of 10 mM concentration of the inhibitors for mild steel corrosion in 1 M H₂SO₄ obtained by weight loss measurements at higher temperatures

Name of the inhibitor	Temperature (K)	Weight loss (g)	Inhibition Efficiency (%)	Corrosion rate (mpy)
Blank	303	0.3849	-	17625.98
	313	0.4270	-	19553.90
	323	0.4556	-	20863.60
	333	0.4698	-	21513.87
THPM 1	303	0.0336	93.1	1538.67
	313	0.0626	85.3	2866.67
	323	0.0716	84.3	3278.40
	333	0.0824	82.5	3773.40
THPM 2	303	0.0249	93.5	1140.26
	313	0.0329	92.3	1506.6
	323	0.0398	91.3	1822.59
	333	0.0485	89.7	2226.99
THPM 3	303	0.0222	94.3	1016.62
	313	0.0279	93.5	1277.64
	323	0.0382	91.6	1749.32
	333	0.0494	89.5	2262.21
THPM 4	303	0.0088	97.7	402.98
	313	0.0176	95.9	805.97
	323	0.0364	92.4	1666.89
	333	0.0142	90.6	2024.08
THPM 5	303	0.0152	97.2	696.06
	313	0.0198	95.4	906.71
	323	0.0355	92.2	1625.68
	333	0.0142	90.6	2024.08
THPM 6	303	0.0021	99.4	96.17
	313	0.0105	97.5	480.83
	323	0.0550	87.9	2518.65
	333	0.0659	86.0	3017.80

Table 5. Inhibition efficiencies of various concentrations of the inhibitors for mild steel corrosion in 1 M H₂SO₄ obtained by gasometric measurements at 30±1 °C

Name of the inhibitor	Concentration (mM)	Gasometric method Inhibition efficiency (%)	AAS method Inhibition efficiency (%)
	Blank	-	-
THPM 1	0.5	82.1	80.9
	5.0	91.1	90.0
	10.0	95.7	92.6
THPM 2	0.5	77.4	73.7
	5.0	89.4	87.8
	10.0	96.6	93.1

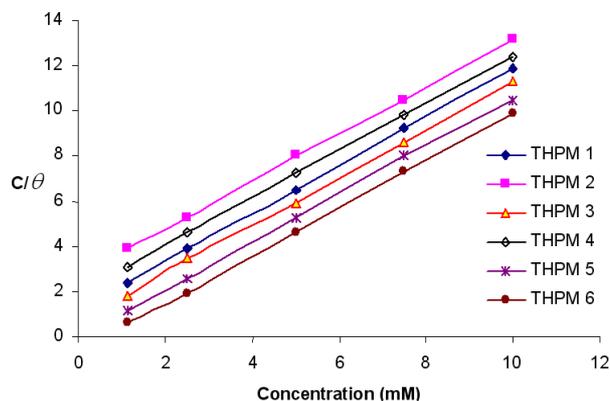


Fig. 2. Langmuir plot of inhibitors

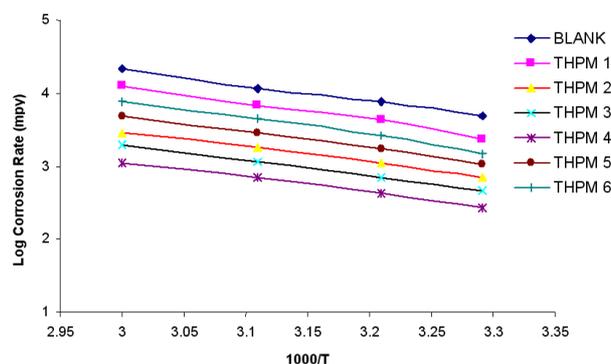


Fig. 3. Arrhenius plot for the corrosion of mild steel in 1 M H₂SO₄ in the absence and presence of inhibitors

efficiency obtained by weight loss method and gasometric method. The percentage of inhibition efficiency obtained by AAS technique was found in good agreement with that obtained from the conventional weight loss method.

The synergistic effect provided by the addition of halide ions, I⁻, Br⁻ and Cl⁻ to the solution containing 1 M H₂SO₄ and the synthesized compounds (THPM 2, THPM 6) were studied by weight loss method and the data are presented in Table 6. Analysis of the data revealed that the synergistic influence of halide ions follows the order, I⁻ > Br⁻ > Cl⁻. The synergism provided by other anions namely sulphates was also studied by weight loss method by the addition of 1 mM zinc sulphate, nickel sulphate and magnesium sulphate to various concentration of the inhibitors THPM 2 and THPM 6 (Table 7). Nickel and magnesium ions were found to exhibit higher synergism in the case of both THPM 2 and THPM 6. Whereas zinc ions reduced the inhibition efficiency of THPM 2 and THPM 6.

The corrosion of mild steel in 1 M H₂SO₄ and its inhibition by the addition of inhibitors was studied by AC - impedance and potentiodynamic measurements. The in-

Table 6. Synergistic effect of 1 mM KCl/KBr/KI on the inhibition of THPM2 and THPM6 by weight loss method at 30±1 °C

Name of the inhibitor	Concentration (mM)	Inhibition efficiency (%)			
		Without KCl, KBr and KI	With 1mM KCl	With 1mM KBr	With 1mM KI
THPM 2	0.5	93.1	95.5	95.9	96.3
	1.0	93.7	96.1	97.2	98.0
	1.5	93.8	96.6	98.8	98.9
	2.0	94.1	97.4	98.3	98.9
	2.5	94.3	98.0	99.1	99.6
THPM 6	0.5	81.3	89.5	90.7	93.8
	1.0	81.8	90.6	92.2	94.3
	1.5	84.1	91.8	94.8	97.1
	2.0	85.9	93.5	95.9	98.2
	2.5	87.4	96.9	98.2	99.9

Table 7. Effect of metal ions on the inhibition of THPM2 and THPM6 by weight loss method at 30±1 °C

Name of the inhibitor	Concentration (mM)	Inhibition efficiency (%)			
		Without Zn, Ni and Mg	With 1mM Zn	With 1mM Ni	With 1mM Mg
THPM 2	0.5	93.1	81.9	99.1	96.9
	1.0	93.7	86.0	99.3	97.8
	1.5	93.8	88.9	99.5	98.5
	2.0	94.1	89.7	99.7	99.2
	2.5	94.3	90.5	99.9	99.5
THPM 6	0.5	81.3	23.5	97.5	97.8
	1.0	81.8	59.4	98.0	98.7
	1.5	84.1	75.2	98.4	99.1
	2.0	85.9	76.9	98.6	99.5
	2.5	87.4	79.7	98.7	99.7

Table 8. AC - Impedance parameters for corrosion of mild steel for selected concentrations of the inhibitors in 1 M H₂SO₄

Name of the inhibitor	Concentration (mM)	R _t (ohm cm ²)	C _{dl} (μF/cm ²)	Inhibition efficiency (%)
THPM 1	Blank	8.28	16.62	-
	0.5	126.28	12.71	93.4
	5.0	138.46	10.35	94.0
	10.0	310.02	8.78	97.3
THPM 2	0.5	33.61	25.64	75.4
	5.0	51.22	17.18	83.8
	10.0	62.38	11.44	86.7
THPM 3	0.5	202.26	19.75	95.9
	5.0	901.12	13.48	99.1
	10.0	1158.06	10.05	99.3
THPM 5	0.5	674.78	15.07	98.8
	5.0	1153.08	11.30	99.3
	10.0	1253.87	9.44	99.3

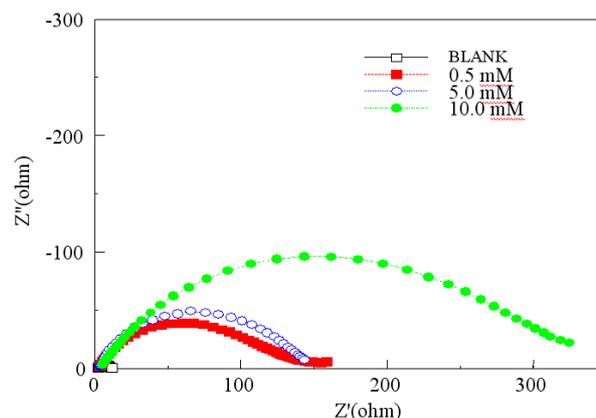
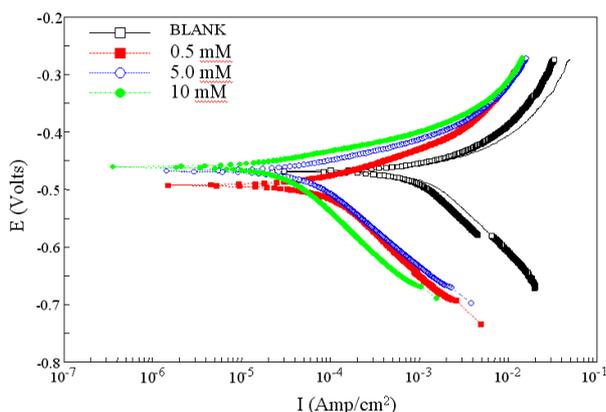


Fig. 4. Nyquist diagram for mild steel in 1 M H₂SO₄ for selected concentrations of inhibitor (THPM 1)

fluence of the inhibitors on the polarization behavior of mild steel was noted which indicates that E_{corr} values are only slightly shifted in the presence of the inhibitors, I_{corr} values decrease with increase in the concentration of the

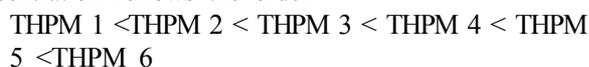
Table 9. Corrosion parameters for mild steel with selected concentrations of the inhibitors in 1 M H₂SO₄ by potentiodynamic polarization method

Name of the inhibitor	Concentration (mM)	Tafel slopes (mV/dec)		E _{corr} (mV)	I _{corr} (μA/cm ²)	Inhibition efficiency (%)
		b _a	b _c			
Blank		149	148	-462	2320	-
THPM 1	0.5	87	145	-493	171.58	92.6
	5.0	87	127	-471	141.98	93.9
	10.0	76	138	-468	74.67	96.8
THPM 2	0.5	127	162	-466	909.82	60.8
	5.0	117	147	-467	562.19	75.8
	10.0	112	127	-456	442.49	80.9
THPM 3	0.5	149	134	-527	244.72	89.4
	5.0	64	126	-418	30.12	98.7
	10.0	62	190	-416	24.37	98.9

**Fig. 5.** Polarization curves for mild steel recorded in 1 M H₂SO₄ for selected concentrations of inhibitor (THPM 1)

inhibitors. The Tafel constants b_a and b_c are both affected but b_a is affected to a greater extent, and b_c to lesser extent. Hence it can be concluded that although all the inhibitors behave as mixed type but they are slightly anodic in nature. This is evident from the results (Table 8 & 9) as shown in Figs. 4 & 5.

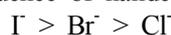
The order of inhibition efficiency of the synthesized compounds at 10 mM concentration follows the order



Substitution of $>C=O$ by $>C=S$ on the pyrimidine ring increases the inhibition efficiency of THPM 2. This may be attributed to the higher electro negativity of 'S' in comparison to oxygen. The higher inhibition efficiency of all the inhibitors is due to the presence of pi electrons and heteroatoms such as nitrogen, oxygen and sulphur which involve greater adsorption of the inhibitor molecules onto the surface of mild steel³⁸⁾ In the case of methoxy sub-

stituted derivatives (THPM 3, THPM 4, THPM 5, THPM 6) it is evident that the inhibition efficiency increases with increase in the number of methoxy groups both at lower and higher concentration. The above results are in accordance with Ita and Offiong³⁹⁾ who have reported that as the number of electron donating substituent on the benzene ring increases the inhibitive power in general increases. By electrochemical method it is evident that the inhibitors behave as mixed type but they are slightly anodic in nature.

The above results also confirm the involvement of the benzene ring in the adsorption process. The synergistic influence of halide ions follows the order.



The higher inhibition efficiency of THPM 2 and THPM 6 in the presence of the Ni²⁺, and Mg²⁺ can be attributed to the formation of a stable complex with the inhibitors which tends to cover the metal surface and protect it from the corrosive environment. Thus the complexes adsorb more effectively on Fe surface and thereby reduce the corrosion rate markedly.⁴⁰⁾ The complex formed by Zn²⁺ with THPM 2, THPM 6 has low stability constant. This is evident from the decrease in the inhibition efficiency of THPM 2, THPM 6 in the presence of Zn²⁺. Probably the complex formed gets desorbed to some extent exposing the mild steel surface to the acidic environment. According to Radovici⁴¹⁾ for the inhibitors which involve in predominant physisorption, inhibition efficiency decreases with increase in temperature. Hence although the inhibitors taken for study can interact with mild steel surface through physisorption and chemisorption mechanism, it is the physisorption mechanism which predominates.

4. Conclusions

- 1) All investigated pyrimidine derivatives are effective

inhibitors for corrosion of mild steel in 1 M H₂SO₄.

2) The adsorption of these inhibitors follows Langmuir adsorption isotherm.

3) Electrochemical impedance spectroscopy experiments show an increase in polarization resistance R_t and a decrease in C_{dl} values, owing to the increased thickness of the adsorbed layer. The Tafel slopes obtained from potentiodynamic polarization curves indicate that they are mixed but slightly anodic in nature.

4) The inhibition efficiency obtained from atomic absorption spectrophotometric studies and gasometric method was found to be in good agreement with that obtained from the conventional weight loss method.

5) Addition of halide ions to the inhibitors THPM 2 and THPM 6 shows an increase in inhibition efficiency. The synergistic influence of halide ion follows the order I⁻ > Br⁻ > Cl⁻. Addition of magnesium ions and nickel ions to the inhibitors THPM 2 and THPM 6 produce synergism while addition of zinc produce antagonistic effect.

6) The inhibition of the compound is governed by physorption mechanism.

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