



Corrosion Inhibition of Mild Steel in Acid Solution by 3,4,5-Trimethoxyphenyl-2-imidazolines

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Abstract: A heterocyclic imidazoline, 3,4,5-trimethoxyphenyl-2-imidazolines (TMP2I) was tested for its corrosion inhibition in 0.5 M H₂SO₄ and 1 M HCl using weight loss, Tafel polarisation and electrochemical impedance techniques. The results show that the inhibition efficiency increases with the increase in concentration of TMP2I and the higher efficiency of about 98% is obtained in both the acid media at 20 ppm. The adsorption of TMP2I obeys Langmuir adsorption isotherm and occurs spontaneously. Cathodic and anodic polarization curves of mild steel in the presence of different concentrations of TMP2I at 30 °C reveal that it is a mixed type of inhibitor. Electrochemical impedance studies reveal that the system follows mixed mode of inhibition. The surface morphology of the mild steel specimens was evaluated using SEM images

Keywords: Mild Steel, 3,4,5-Trimethoxyphenyl-2-imidazolines, Acid inhibition, Polarisation, EIS, SEM

Introduction

Corrosion problems have received a considerable amount of attention because of their attack on materials. The use of inhibitors is one of the most practical methods for protection against corrosion. Many researchers have studied the influence of organic compounds containing nitrogen on the corrosion of steel in acid media¹⁻⁹, most organic inhibitors act by adsorption on the metal surface. Corrosion inhibitors function by interfering with either the anodic or cathodic reactions or both. Many of these inhibitors are organic compounds containing nitrogen, sulphur or oxygen atoms or N-heterocyclic compounds¹⁰.

In the present work, we have investigated the inhibitive action of TMP2I on corrosion of mild steel in 0.5 M H₂SO₄ and 1 M HCl using weight loss, Tafel polarisation and electrochemical impedance techniques were carried out. The effects of temperature, immersion time were also studied. Several isotherms were tested for their relevance to describe the adsorption behaviour of the compound studied.

Experimental

TMP2I was synthesized using the procedure described by Midori *et al.*¹¹ and the compound was characterized by IR spectral data. IR spectral data shows broad singlet at 3379.65 cm^{-1} for N-H stretching, aromatic C-H stretching at 2919.96 cm^{-1} , aliphatic stretching at 2827.42 cm^{-1} , C=N stretching at 1636.13 cm^{-1} and for Ar-O-CH₃ stretching at 1227.62 cm^{-1} . The structure of the TMP2I is shown in the Figure 1.

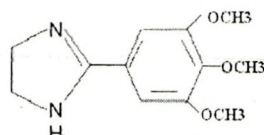


Figure 1. Structure of 3,4,5-trimethoxyphenyl-2-imidazoline

Tests were performed on mild steel having composition (wt.%) C=0.098%, Mn=0.201%, P=0.020%, S=0.016%, Ni=0.012% and Fe=99.653% used for the measurement of the corrosion rates. Rectangular specimens of working surface area $5 \times 1\text{ cm}^2$ were used for weight loss measurements and $1 \times 1\text{ cm}^2$ with 5 cm long stem (isolated with Teflon tape) for the electrochemical methods. The specimens were polished mechanically using emery papers and worked thoroughly with triple distilled water, degreased with acetone and dried using air flow at room temperature.

The electrochemical studies were carried out using a three electrode cell assembly at room temperature. Mild steel coupons of $1\text{ cm} \times 1\text{ cm}$ (exposed area) were used for electrochemical measurements. Platinum was used as counter electrode and saturated calomel electrode as reference electrode. The electrochemical measurements were carried out using Solartron Electrochemical Analyser Model (1280B). The impedance measurements were carried out in the frequency range of 10 kHz to 10 mHz at the rest potential by applying a 5 mV sine wave ac voltage. The same cell and instrument as in the polarization method were used. The double layer capacitance (Cdl) and charge transfer resistance (Rct) were obtained from Nyquist plots.

Results and Discussion

The weight loss obtained for the mild steel in different concentrations of sulphuric acid and hydrochloric acid solution is plotted as concentration vs. IE (%) for various time immersion are shown in Figure 2

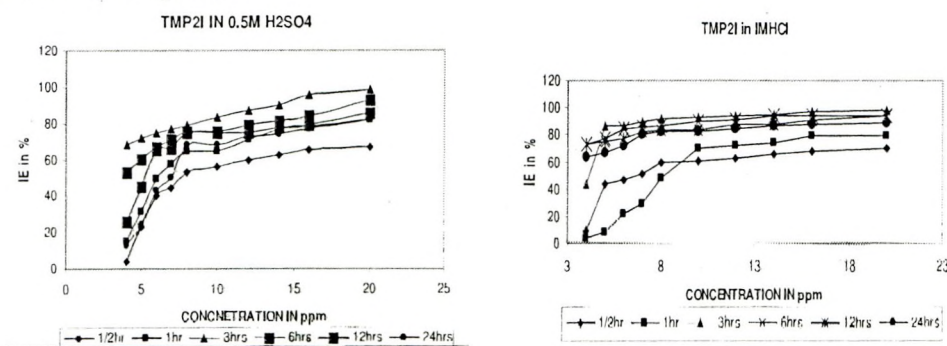


Figure 2. Effect of concentration and immersion time against inhibitor efficiency

From the Figure it can be seen that the inhibition efficiency increases with increase in concentration of TMP2I which suggest that inhibition is a result of adsorption of inhibitor on the metal surface and TMP2I acts as an adsorption inhibitor. The reason for the high efficiency of the inhibitor may be due to the nitrogen atom in TMP2I molecule^{12,13}.

Influence of temperature on TMP2I corrosion in 0.5 M H₂SO₄ and 1M HCl

The influence of temperature on the corrosion behaviour of steel at various concentrations is investigated in the temperature range 303-343K. The variation of inhibition efficiency with temperature in both the acid media is as shown in the Figure 3

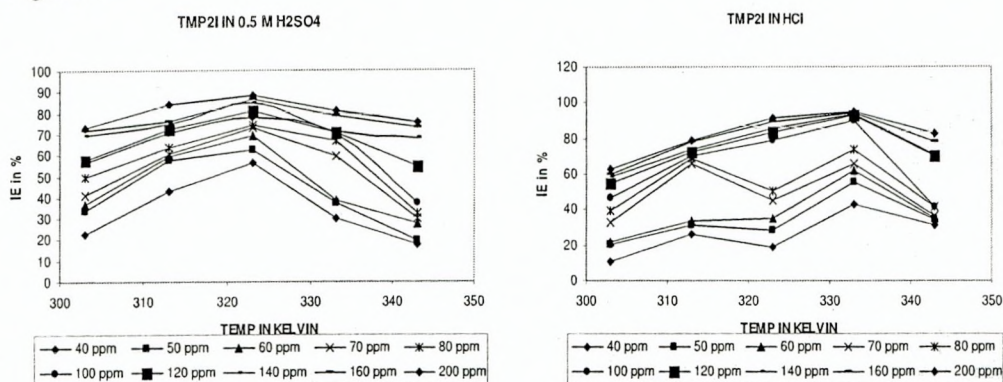


Figure 3. Effect of temperature on the inhibitor efficiency of TMP2I in acid media

From the Figure it can be deduced that an increase in the temperature range of 303-343 K enhanced the IE of the inhibitor up to 333 K in HCl medium and 313 K in sulphuric acid medium.

The behaviour of TMP2I at 303 K may be attributed to the adsorption of the inhibitor up to 313 K and after that further increase in temperature brings about desorption of the TMP2I under study. This may be explained as follows. Adsorption and desorption of inhibitor molecules continuously occur at the metal surface and the equilibrium exists between these two processes at a particular temperature, with the increase of temperature, the equilibrium between adsorption and desorption process is shifted leading to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant. It explains the lower IE at higher temperature¹⁴.

Adsorption isotherms

Surface coverage data play an important role in assessment of inhibitor characteristics and are useful for fitting experimental data in to adsorption isotherms which give detailed insight into the inhibition mechanism. TMP2I obeys Langmuir and Temkin adsorption isotherms by giving a straight line for a plot of $\log C$ vs. $\log \theta/1-\theta$ and $\log C$ vs. θ respectively. These straight lines obtained reveal that the main process of inhibition is adsorption.

Thermodynamic parameters

The values of free energy of adsorption were calculated using the standard equation¹⁴. The results obtained are given in Table 1.

Table 1. Thermodynamic parameters for mild steel in the presence and absence of TMP2I in H₂SO₄ and HCl

Conc in ppm	HCl								H ₂ SO ₄							
	-Ea	Change in Free energy					-ΔS J/mole	ΔH kJ/mole	Ea	Change in Free energy					-ΔS J/mole	ΔH kJ/mole
	303	313	323	333	343			303	313	323	333	343				
40	43	7	10	9	12	10	87	18	42	9	12	13	10	8	30	20
50	42	8	10	9	13	11	101	72	46	10	13	13	10	9	50	27
60	41	8	11	10	14	11	115	14	47	10	12	13	12	9	23	19
70	48	9	14	10	14	11	90	21	42	10	12	13	13	10	14	38
80	47	9	14	11	15	11	106	35	44	10	12	13	13	11	24	44
100	40	10	15	13	18	11	72	25	46	11	12	13	12	9	40	33
120	40	10	15	11	19	15	13	86	46	11	12	13	12	12	11	41
140	30	10	15	12	19	15	14	25	47	11	12	13	12	13	32	55
160	26	9	16	12	20	16	16	66	40	12	12	13	12	14	44	87
200	22	9	16	12	20	16	18	25	40	12	12	14	12	15	58	88

It was found that the ΔG_{ads} value is less than -20 kJ/mol indicating that the TMP2I are physically adsorbed on the metal surface¹⁵⁻¹⁸. The negative value of ΔG_{ads} shows a strong interaction of inhibitor molecules and a spontaneous adsorption of inhibitor on the surface of the mild steel^{16,20}. Generally values of ΔG_{ads} up to -20 kJ/mol are consistent with electrostatic interaction between charged molecule and a charged metal (which indicates physisorption) while those more negative than -40 kJ/mol involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond which indicated Chemisorption¹⁹⁻²¹. Physical adsorption is a result of electrostatic attraction between charged species in the bulk of the solution. The higher values of ΔH in the presence of inhibitor indicate higher protection efficiency of the inhibitor. The positive values of ΔH suggest that the dissolution process is an exothermic phenomenon and the dissolution of steel is difficult. This means the formation of an ordered stable layer of inhibitor on mild steel²². The values of entropy prove strong interaction of the inhibitor on the metal surface²³.

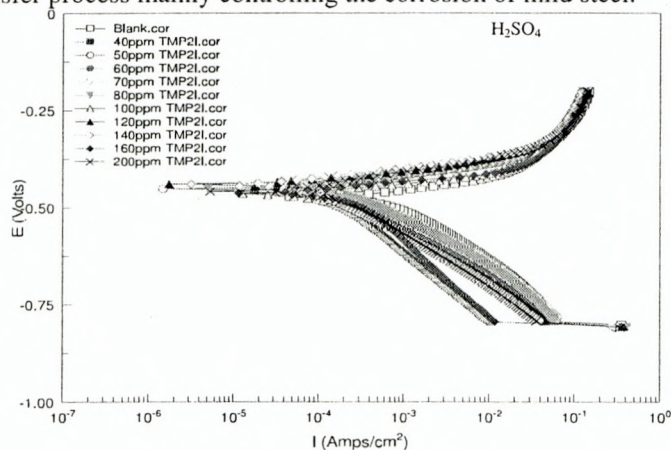
The Activation energy of the inhibited solution decreases by increasing the concentration of the inhibitor. This finding indicates that TMP2I retards the corrosion of mild steel in both examined media²⁴. Thermodynamic parameters for mild steel in the presence and absence of TMP2I are presented in the Table 1.

Tafel polarisation

Polarisation curves for mild steel in H_2SO_4 and HCl at various concentrations of TMP2I are presented in Figure 4. The values of corrosion current densities (I_{corr}), corrosion potential (E_{corr}), the anodic Tafel slope ba and cathodic tafel slope bc presented in Table 2. The presence of TMP2I does not remarkably shift the corrosion potential (E_{corr}) and hence said to be mixed type of inhibitor.

EIS measurements

Nyquist plots of mild steel at various concentration of TMP2I in acid media are presented in Figure 5. All the Nyquist plots obtained were in semicircle in nature and the diameter of the semicircles were changed with change in inhibitor concentration. The obtained semicircle cut the real axis at higher and lower frequencies. At higher frequency end, the intercept corresponds to R_s solution resistance and at lower frequency end corresponds to R_s+R_{ct} . The difference between the two values gives R_{ct} , the charge transfer resistance. The value of R_{ct} is a measure of the electron transfer across the surface and is inversely proportional to corrosion rate¹². The semicircle indicates the formation of a barrier on the surface and a charge transfer process mainly controlling the corrosion of mild steel.



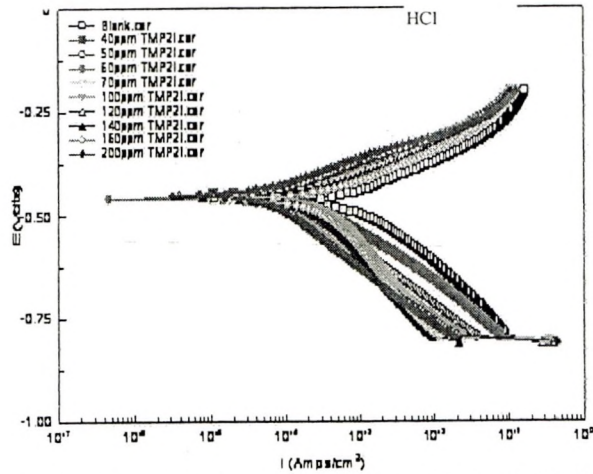


Figure 4. Polarisation curves for mild steel for mild steel in H_2SO_4 and HCl

Table 2. Results of polarisation studies of mild steel in the presence of TMP2I in H_2SO_4 and HCl

Conc of TMP2I in ppm	I_{corr}	E_{corr}	ba	bc	IE %	
	$\times 10^{-4}$ mA/cm ²	mV/sec	mV/dec	mV/dec		
H_2SO_4	Blank	8.76	475	73	159	
	40	1.96	449	53	110	77.62
	50	1.73	451	52	105	0.20
	60	1.49	456	52	105	82.99
	70	1.24	465	51	129	85.80
	80	1.12	457	50	115	87.21
	100	1.01	451	49	87	88.40
	120	0.72	471	49	116	91.70
	140	0.46	442	44	95	94.64
	160	0.21	453	46	70	97.50
	200	0.21	442	40	74	97.51
HCl	Blank	0.650	463	79	122	
	40	0.568	449	62	140	12.60
	50	0.467	449	64	132	28.10
	60	0.324	457	78	221	50.15
	70	0.289	459	75	224	55.5
	100	0.211	453	71	218	67.5
	120	0.165	455	67	177	74.61
	140	0.112	440	65	104	82.76
	160	0.100	449	68	131	84.61
	200	0.077	456	69	142	88.13

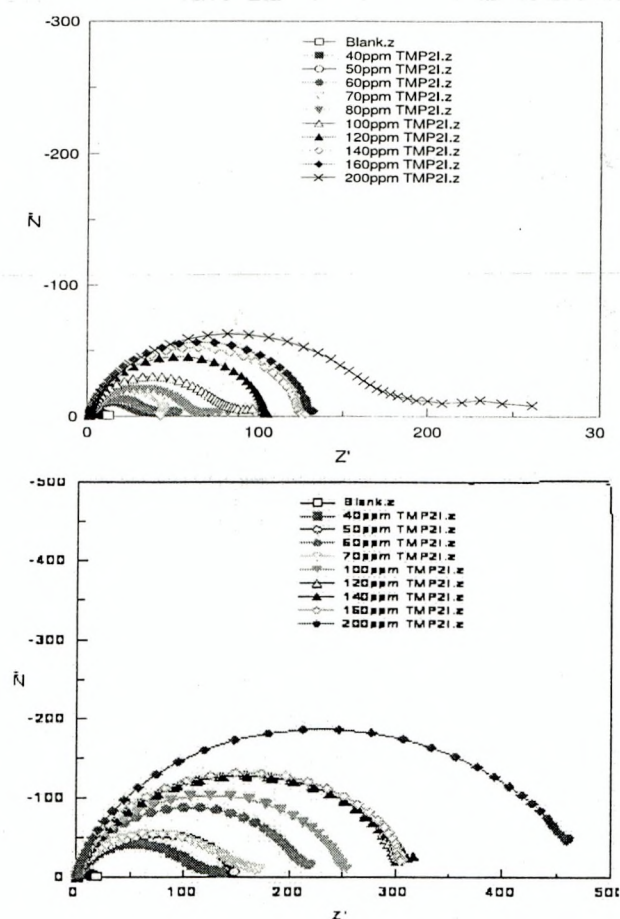


Figure 5. Impedance diagram of mild steel in the presence of TMP2I in acid media

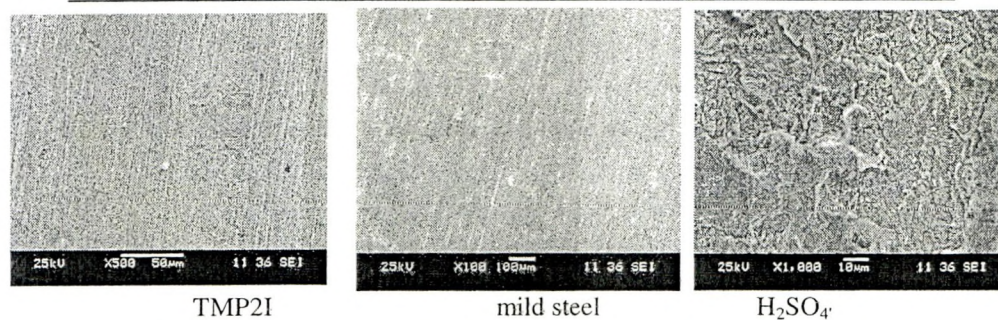
The impedance parameters like R_{ct} , R_p , C_{dl} and IE are presented in Table 3. The results also show that R_{ct} values increased with increase in increase concentration of the inhibitor. The percentage inhibition calculated form R_{ct} values indicated that TMP2I acts as good inhibitor in both acid media. The C_{dl} values found to decrease with increase in concentration of inhibitor solutions. This behaviour is generally seen for system where inhibition occurred due to the formation of a layer by the adsorption of inhibitor on the metal surface. The decrease in C_{dl} value suggest that the inhibitor molecule act by adsorption at the metal solution interface²⁶.

Scanning electron microscopic studies

Figure 6 shows the SEM images of mild steel surface after immersed in 0.5 M H_2SO_4 in the absence and presence of TMP2I. Close examination of the SEM images revealed that the specimens immersed in the inhibitor solutions are in better conditions with smooth surfaces compared with those of corroded rough and coarse uneven surfaces of mild steel immersed in 0.5 M H_2SO_4 alone. This observation indicated that corrosion rate is reduced to a very low value in the presence of the inhibitors. This might be due to the adsorption of inhibitor molecule on the metal surface as a protective layer²⁶.

Table 3. Corrosion kinetic parameters of mild steel in the presence of TMP2I in H₂SO₄ and HCl

Conc in ppm	Rp		Rct		Cdl x 10 ⁻⁴		Θ
	ohm/cm ²	IE %	ohm/cm ²	IE %	μF/cm ²		
Blank	25.59		7.94		2.22		
40	78.13	67.24	29.92	73.45	2.43	0.094	
50	80.49	68.20	34.14	76.74	2.74	0.234	
60	82.47	68.97	34.98	77.30	3.05	0.373	
70	83.42	69.32	45.67	82.61	2.88	0.297	
80	86.41	70.38	59.33	86.6	1.36	0.387	
100	88.80	71.18	77.24	89.72	1.31	0.409	
120	91.24	71.95	103.57	92.33	1.21	0.423	
140	140.76	81.82	123.97	93.59	1.28	0.454	
160	175.96	85.45	129.69	93.87	0.73	0.670	
200	249.41	89.73	183.26	95.66	0.66	0.892	
Blank	29.64		13.57		1.97		
40	2978.	62.10	112.99	88.00	1.18	0.400	
50	88.60	66.50	147.60	90.80	0.89	0.546	
60	116.01	74.40	153.27	91.11	0.80	0.590	
HCl 70	123.55	76.00	211.28	93.60	0.78	0.600	
100	140.76	78.94	250.40	94.60	0.78	0.602	
120	189.08	84.32	311.37	95.65	0.69	0.647	
140	243.81	87.84	313.77	95.69	0.68	0.653	
160	288.63	89.70	316.99	95.73	0.60	0.691	
200	359.44	91.75	461.77	97.07	0.60	0.691	

**Figure 6.** SEM of TMP2I, mild steel and mild steel dipped in H₂SO₄

Conclusion

TMP2I has been found to be a good inhibitor for mild steel in both the acid media. Inhibition efficiency varies linearly with concentration. The optimum concentration of the inhibitor found is 200 ppm. The inhibitor acts as mixed type inhibitor. The results obtained from weight loss, polarization and EMS methods match one another. The inhibitors obey Langmuir adsorption and Temkin adsorption isotherms.

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