

Effect of New Synthesised Pyridazine Derivatives on the Electrochemical Behaviour of Mild Steel in 1M HCl Solution: Part-1

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The effect of adding new pyridazine derivatives, ethyl [4-(2-chlorobenzyl)-3-methyl-6-oxopyridazin-1(6H)-yl]acetate (P1), ethyl [4-(2-chlorobenzyl)-3-methyl-6-thioxopyridazin-1(6H)-yl]acetate (P2), 5-(2-chlorobenzyl)-2-(2-hydroxyethyl)-6-methylpyridazin-3(2H)-one (P3) and 5-(2-chlorobenzyl)-2-(2-hydroxyethyl)-6-methylpyridazine-3(2H)-thione (P4), on the electrochemical behaviour of steel in molar hydrochloric acid was investigated by using weight loss method, potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) measurements. Results reported in this study show that the addition of these compounds inhibits the corrosion of steel and the extent of inhibition depends upon the type and concentration of the pyridazine compounds. The inhibition efficiency for four compounds studied increase with the increase in the inhibitor concentrations to attain 100% at the 10⁻³M of P1. Moreover, Potentiodynamic polarisation studies revealed that the inhibitors act as mixed inhibitors and cathodically predominant. The inhibition occurs through adsorption of the pyridazine compounds on the metal surface without modifying the mechanism of corrosion process. EIS study shows that charge transfer resistance increases with the inhibitor concentration. Effect of temperature is studied between 303 and 353 K and determination of activation and adsorption parameters is also discussed in part 2. Explanation by quantum indices to correlate inhibition efficiency should be given in part 3.

Keywords: Corrosion inhibitor; Comparative study; Pyridazine derivatives; Mild steel, Hydrochloric acid.

1. INTRODUCTION

Mild steel has been widely used in many chemical industries due to its low cost and easy availability for fabrication of reaction vessels, tanks and pipes... Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes.

Inhibitors are generally used to control metal dissolution. The inhibition of corrosion in acid solutions can be secured by the addition of a variety of organic compounds and has been investigated by several workers [1-21]. Most of the well-known acid inhibitors are organic compounds containing Nitrogen, Sulphur and Oxygen atoms [22-26]. However, the use of organic inhibitors in acid solutions can, in some cases, lead to enhancement of the metal corrosion [27], and stimulation of corrosion is related not only to the type and structure of the organic molecule but also depends on the type of acid and its concentration [11]. For example, the isomers of aminophenol inhibit the corrosion of mild steel in 1M HCl and accelerate it in 0.5M H₂SO₄ [28].

There are various organic inhibitors which tend to decrease the corrosion rate of steel and iron in acidic solutions. These substances in general, are effective through adsorption on the metal surface. The corrosion inhibition by some pyridazines derivatives has been studied by several researchers [29-32]. Results obtained show that they act as cathodic inhibitors without modifying the mechanism of hydrogen evolution and the adsorption of inhibitors is explained by an intramolecular synergistic effect of pyridazine and substituents.

In the present paper, four pyridazines derivatives were newly synthesized and tested as corrosion inhibitors for mild steel in 1M HCl using gravimetric measurement, potentiodynamic polarization methods and electrochemical impedance spectroscopy. A comparative inhibition study was investigated and studied. Effect of temperature is studied between 303 and 353 K and determination of activation and adsorption parameters is also discussed in part 2. Explanation by quantum indices to correlate inhibition efficiency should be given in part 3.

2. EXPERIMENTAL PART

The aggressive solution (1M HCl) was prepared by dilution of analytical grade 37% HCl with bidistilled water. Prior to all measurements, the steel samples were polished with different emery paper up to 1200 grade and washed thoroughly with bidistilled water and dried with acetone. The chemical structures of the studied pyridazine derivatives are given in Fig. 1. The chemical synthesis procedure is:

P 1 : Ethyl [4-(2-chlorobenzyl)-3-methyl-6-thioxopyridazin-1(6H)-yl]acetate .

To a 1 mmole of pyridazinone was added 2 mmoles of pentasulfurphosphorus. The mixture was placed in a pyrex tube which was then introduced into a Maxidigest MX 350 Prolabo microwave monomode reactor fitted with a rotational system. At the end of the irradiation time (10 min on 90 w as

irradiation power), to a mixture was added 5 ml of hot water, the residues was filtered and recrystallized with ethanol to give the compound P4.

Melting point: 105- 108°C

RMN ¹H (300.14 MHz, CDCl₃) δ (ppm): 1,30 (t, 2H, CH₃); 2,39 (s, 3H, CH₃); 3,88 (s, 2H, CH₂) 4,281(q, 2H, CH₂); 5,31 (s, 2H, CH₂); 7,13 (m, 3H, H_{ph}); 7,15 (s, 1H, H₄); 7,19 (m, 1H, H_{ph}).

RMN ¹³C (75 MHz, CDCl₃) δ (ppm): 14,12 (CH₃); 19,16 (CH₃); 34,87 (CH₂); 59,72 (CH₂); 61,87 (CH₂); 127,51 (CH -ph); 129,22 (CH -ph) ;130,13 (CH -ph); 130,13 (CH -ph), 131,15 (CH -ph); 133,20; 134,37; 137,48; 140,71 (CH); 150,03; 166,34 (C=O); 179,46 (C=S).

IR (KBr, cm⁻¹): 1760 (C=O); 1610 (C=N), 1510, 1410, 1210 (C = N),1190 (C=S)

SM m/z (%) : 336,5 (M⁺); 291; 265; 263.

P2 : Ethyl [4-(2-chlorobenzyl)-3-methyl-6-oxopyridazin-1(6H)-yl]acétate .

The product P3 was prepared from 5-(2-chlorobenzyl)-6-methylpyridazin-3(2H)-one in situ by the solid-liquid PTC conditions without solvent[3]. To pyridazin (1.2 g, 6 mmol) was added (2.75 g, 9 mmol) of potassium carbonate, (0.3 g, 1 mmol) of TBAB and (1 g, 6 mmol) of 2-ethyl bromoacetate. The mixture was placed in a pyrex tube which was then introduced into a Maxidigest MX 350 Prolabo microwave monomode reactor fitted with a rotational system. At the end of the irradiation time (10 min on 90 w as irradiation power), the mixture was cooled to ambient temperature. After elution with ethyl acetate (30 ml) and subsequent filtration on florisil, the organic product was purified by chromatography on silicagel using CH₂Cl₂ as eluent, yield : 962% of P3 solid.

Melting point: 89-90°C

IR (KBr, cm⁻¹): 1747 (CO₂Et), 1670 (C=O), 1605, 1470, 1210 (C = N)

¹H-NMR (300.14 MHz, CDCl₃) δ (ppm): 1.28 (t, J = 7.5 Hz, 3H, CH₃), 2.31(s, 3H, CH₃), 3.38 (s, 2H, CH₂), 4.25 (q, J = 5 Hz, 2H, CH₂), 4.82 (s, 2H, CH₂), 6.32 (s, 1H, H₄), 7.20 (m, 4H, H-ph).

¹³C-NMR (75 MHz, CDCl₃) δ (ppm):14.11 (CH₃), 19.03 (CH₃) 35.77 (CH₂), 52.68 (CH₂), 61.66 (CH₂), 127.71 (CH o), 127.42(CH -ph), 129.02 (CH -ph), 130.02 (CH -ph), 131, 12 (CH-ph) 134.43, 144.97, 145.17, 160.30 (C3) ,167.72 (C=O).

SM m/z (%) (M+1)⁺ = 321.5, 279, 275,219.

P-3: 5-(2-chlorobenzyl)-2-(2-hydroxyethyl)-6-methylpyridazin-3(2H)-one

The product P2 was prepared from 5-(2-chlorobenzyl)-6-methylpyridazin-3(2H)-one in situ by the solid-liquid PTC conditions without solvent. To pyridazin (1.2 g, 6 mmol) was added (2.75 g, 9 mmol) of potassium carbonate, (0.3 g, 1 mmol) of TBAB and (1 g, 6 mmol) of 2- bromoethanol. The mixture was placed in a pyrex tube which was then introduced into a Maxidigest MX 350 Prolabo microwave monomode reactor fitted with a rotational system. At the end of the irradiation time (10 min on 90 w as irradiation power), the mixture was cooled to ambient temperature. The product was recrystallized in ethanol and filtered to give P2 solid.

yield 90% .

Melting point: 70°C

$^1\text{H-NMR}$ (300.14 MHz, CDCl_3) δ (ppm): 2.35 (t, , 3H, CH_3), 3.9 (s, 2H, CH_2), 4.00 (t, , 2H, CH_2), 4.35 (t, 2H, CH_2), 6.35 (s, 1H, H4), 7.20 (m, 2H, Hph); 7,30(1H,Hph) ; 7,45(1H,Hph)

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ (ppm): 19.2 (CH_3), 19.03 (CH_3) 35.77 (CH_2), 54.50 (CH_2-N_2), 61.53 (CH_2-OH), 127.50 (C-4), 127.56, 129.017 , 130.13 , 131, 26 (3 Cph) 133.84(C-Cl), 134.5(C- CH_2), 144.90, 145.30, 161.58 (C3) .

P-4: 5-(2-chlorobenzyl)-2-(2-hydroxyethyl)-6-methyl-3-thiopyridazin (2H)

The product P4 was prepared from 5-(2-chlorobenzyl)-2-(2-hydroxyethyl)-6-methylpyridazin-3(2H)-one P3 (0.035mol) To a 0.035 mole of P3 was added 20.065 moles of pentasulfurphosphorus. The mixture was placed in a pyrex tube which was then introduced into a Maxidigest MX 350 Prolabo microwave monomode reactor fitted with a rotational system. At the end of the irradiation time (10 min on 90 w as irradiation power), to a mixture was added 5 ml of hot water ,the residues was filtered and recrystallized with ethanol to give the compound P4.

yield 85 % .

Melting point: 163°C

$^1\text{H-NMR}$ (300.14 MHz, CDCl_3) δ (ppm): 2.38 (s, , 3H, CH_3), 3.95 (2H, CH_2), 4.20 (t, , 2H, CH_2), 4.40 (t, 2H, CH_2), 6.38 (s, 1H, H4), 7.30 (m, 2H, Hph); 7,40(1H,Hph) ; 7,49 (1H,Hph)

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ (ppm): 19.4 (CH_3), 35.87 (CH_2), 54.56 (CH_2-N_1), 61.53 (CH_2-OH), 127.56 (C-4), 127.59, 129.18, 130.134, 131, 28 (4 Cph) 133.90(C-Cl), 134.55(C- CH_2), 144.94C-4), 145.70(C-9), 192.58 (C=S) .

Gravimetric measurements were carried out in a double-walled glass cell equipped with a thermostat cooling condenser. The solution volume was 100 ml. The steel specimens used had a rectangular form (2cm \times 2cm \times 0.05cm). The immersion time for the weight loss was 6 h at 308 K.

Electrochemical measurements were conducted in a conventional three-electrode cylindrical glass cell at 308 \pm 1 K with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode. The working electrode (WE) had the form of a disc cut from the steel sheet. The area exposed to the corrosive solution was 1 cm².

Electrochemical experiments were recorded by using an EG&G potentiostat, model 263A, coupled to a computer equipped with a software 352 Soft Corr III. Before recording the polarisation curves, the test solution was de-aerated and magnetically stirred for 30 min in the cell with pure nitrogen. Gas pebbling was maintained throughout the experiments.

The working electrode was then inserted and prepolarised at -800 mV (SCE) for 10 min in order to remove oxide film from the electrode and E_{corr} was monitored until stationary (30 min). The scan rate was 1 mV/s.

For electrochemical impedance spectroscopy (EIS), after the determination of steady-state current at a given potential, sine wave voltage (10 mV) peak–peak, at frequencies between 100 kHz and 10 mHz were superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure. The impedance diagrams are given in the Nyquist representation.

Pyridazine name	Chemical Structure	Abbreviation
ethyl [4-(2-chlorobenzyl)-3-methyl-6-oxopyridazin-1(6H)-yl]acetate		P1
ethyl [4-(2-chlorobenzyl)-3-methyl-6-thioxopyridazin-1(6H)-yl]acetate		P2
5-(2-chlorobenzyl)-2-(2-hydroxyethyl)-6-methylpyridazin-3(2H)-one		P3
5-(2-chlorobenzyl)-2-(2-hydroxyethyl)-6-methylpyridazine-3(2H)-thione		P4

Figure 1. Chemical names, structures of the pyridazine derivatives and their abbreviation

3. RESULTS AND DISCUSSION

3.1. Gravimetric measurements

The effect of all addition of P1, P2, P3 and P4 at different concentrations on mild steel corrosion in 1M HCl solution was studied by weight loss measurement at 6 h of immersion. Table 1 gathers the values deduced of W_{corr} and the inhibition efficiency ($E_w\%$) determined by the following equation:

$$E_w \% = \left(1 - \frac{W_{\text{corr}}}{W_{\text{corr}}^{\circ}} \right) \times 100 \quad (1)$$

Where W_{corr} and W_{corr}° are the corrosion rates of mild steel in the presence and absence of each inhibitor, respectively.

Table 1 indicates clearly a decrease in the corrosion rate in the presence of all products. This effect is hugely marked at higher concentration of inhibitors. The inhibition efficiency followed the following order:

$$P1 > P2 \approx P4 > P3$$

The presence of P1 gave a high inhibiting efficiency followed by P4. This is probably due to the presence of sulphur and nitrogen atom according to Every and Riggs [33], the organic compound containing the nitrogen and sulphur has better inhibition efficiency, in acidic media, compared to the organic compound containing nitrogen or sulphur. In addition, the comparison of P1 and P4 ($P1 > P4$), the both product has a sulphur atom in its structure, the alone difference is the presence of oxygen in position 5 for P1, this oxygen atom make easier the formation of a stable complex with Fe^{2+} ions. The aim of this oxygen atom in position 5 can be showed in the comparison of P1 and P4. These explanations are confirmed by P3, when we note the absence of sulphur and oxygen atoms in position 5 leading lower inhibition efficiency for this product.

Table 1. Gravimetric results of mild steel in 1M HCl at different concentration of each inhibitor at 6h and 303 K.

Inhibitors	Concentration (M)	W_{corr} (mg/cm ² .h)	E_w (%)
Blank	1	1.15	–
P1	10^{-6}	0.55	52
	10^{-5}	0.46	60
	5×10^{-5}	0.31	73
	10^{-4}	0.19	83
	5×10^{-4}	0.034	97
	10^{-3}	0.001	100
P2	10^{-6}	0.57	51
	10^{-5}	0.50	56
	5×10^{-5}	0.35	70
	10^{-4}	0.23	80
	5×10^{-4}	0.10	91
	10^{-3}	0.089	92
P3	10^{-6}	0.58	50
	10^{-5}	0.53	53
	5×10^{-5}	0.40	65
	10^{-4}	0.28	76
	5×10^{-4}	0.16	86
	10^{-3}	0.13	89
P4	10^{-6}	0.525	53
	10^{-5}	0.48	58
	5×10^{-5}	0.34	70
	10^{-4}	0.23	80
	5×10^{-4}	0.098	92
	10^{-3}	0.092	92

3.2. Polarization curves

The polarization curves of mild steel in 1M HCl obtained with and without various concentrations of used inhibitors are shown in Fig.2. Electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), Tafel slope constants calculated from Tafel plots ($-\beta_c$) and the inhibition efficiency (E_I %) were determined by Tafel extrapolation method and are given in Table 2. E_I % was calculated using the equation 2:

$$E_I \% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \tag{2}$$

Where I_{corr} and $I_{corr(inh)}$ are the corrosion current density values without and with inhibitor, respectively.

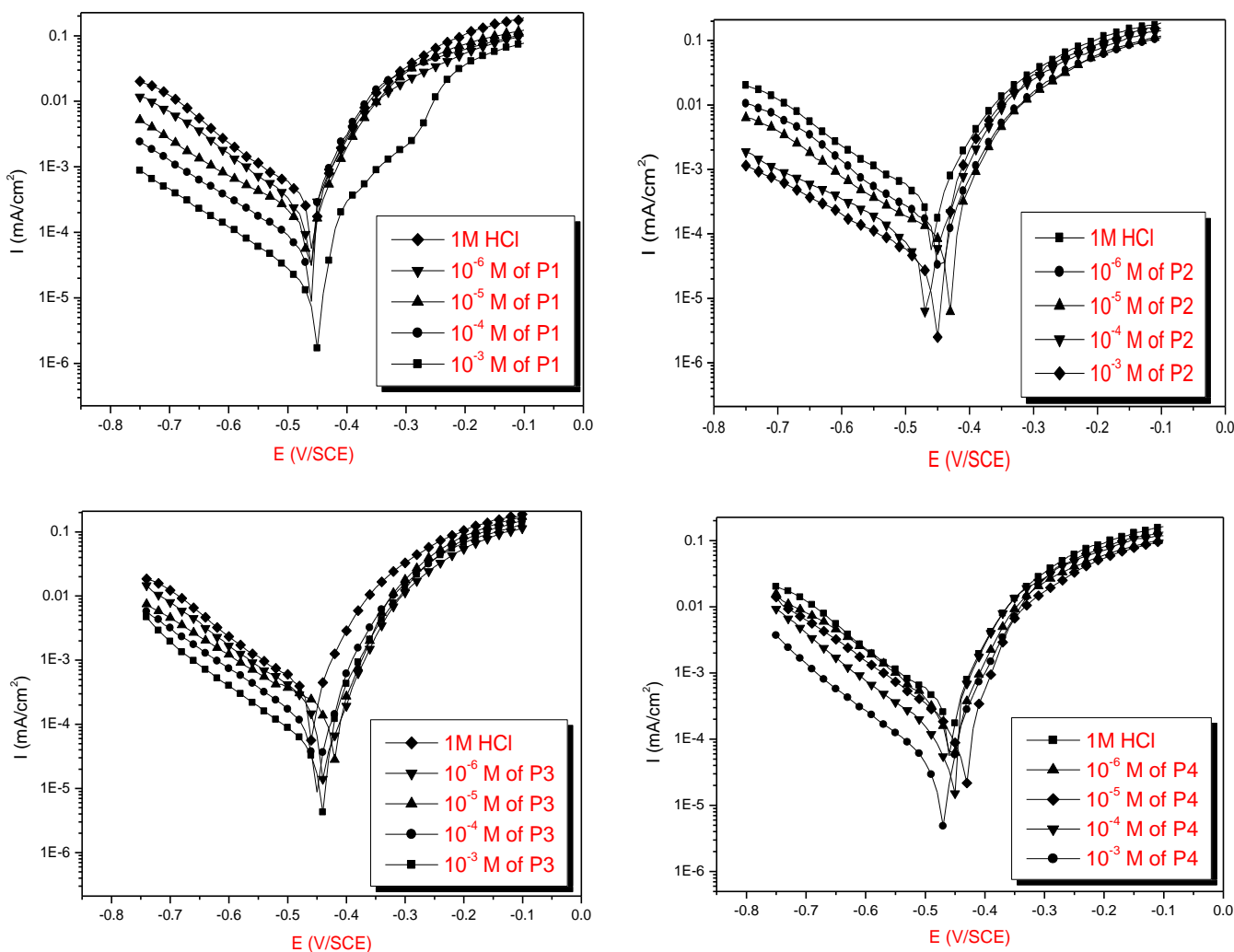


Figure 2. Polarization curves of mild steel in 1M HCl containing different concentrations of P1, P2, P3 and P4

It is seen that the addition of various inhibitors affects the polarization curves and consequently decreases I_{corr} significantly, due to increase in the blocked fraction of electrode surface by adsorption. Cathodic curves gave rise to parallel Tafel lines indicating that the hydrogen evolution is activation controlled and the reduction mechanism is not affected by the presence of inhibitors. In another hand, we note that the addition of products did not change the corrosion potential values (E_{corr}) for all concentration. These results demonstrated that the hydrogen evolution reaction was inhibited and that the inhibition efficiency increased with inhibitor concentration.

In the anodic domain, the presence of two inhibitors decreases anodic current density, the highest effect is observed with P1 and P3 increase of the over voltage near the corrosion potential. For an over voltage higher than -200 mV/SCE, the presence of this inhibitors does not change the current density-potential characteristics. This fact means that the inhibition mode of the pyridazines depends upon electrode potential.

The polarization method is good agreement with inhibition efficiency obtained from the weight loss method and the order is always: P1 > P2≈P4 > P3

Table 2. Polarization data of mild steel in 1M HCl without and with addition of inhibitors at 303 K

Inhibitors	Concentration (M)	E_{corr} (mV/SCE)	$-\beta_c$ (mV/dec)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_1 (%)
Blank	1	-460	160	350	–
P1	10^{-6}	-460	160	195	45
	10^{-5}	-460	180	100	72
	10^{-4}	-465	180	45	88
	10^{-3}	-450	185	15	96
P2	10^{-6}	-450	150	170	51
	10^{-5}	-440	154	120	66
	10^{-4}	-460	180	60	83
	10^{-3}	-450	186	36	90
P3	10^{-6}	-440	165	172	51
	10^{-5}	-430	170	100	72
	10^{-4}	-450	180	66	81
	10^{-3}	-450	155	42	88
P4	10^{-6}	450	166	218	38
	10^{-5}	440	162	106	70
	10^{-4}	450	160	59	83
	10^{-3}	460	160	35	90

3.3. Electrochemical impedance spectroscopic studies

The corrosion behaviour of mild steel, in acidic solution containing different concentration of pyridazine compounds, was investigated by the electrochemical impedance spectroscopy (EIS) at 303

K after 30 min of immersion. The obtained results are presented in Fig.3. The impedance parameters calculated are given in Table 3. The diagrams are composed of one capacitive loop. The charge-transfer resistance values (R_{ct}) were calculated from the difference in real impedance at lower and higher frequencies as suggested by Tsuru et al. [34]. To obtain the double-layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum ($-Z_{i_{max}}$) is found and C_{dl} values were obtained from the equation 3:

$$f(-Z_{max}) = \frac{1}{2\pi C_{dl} R_{ct}} \tag{3}$$

In this case, the inhibition efficiency is calculated using charge transfer resistance from equation 4:

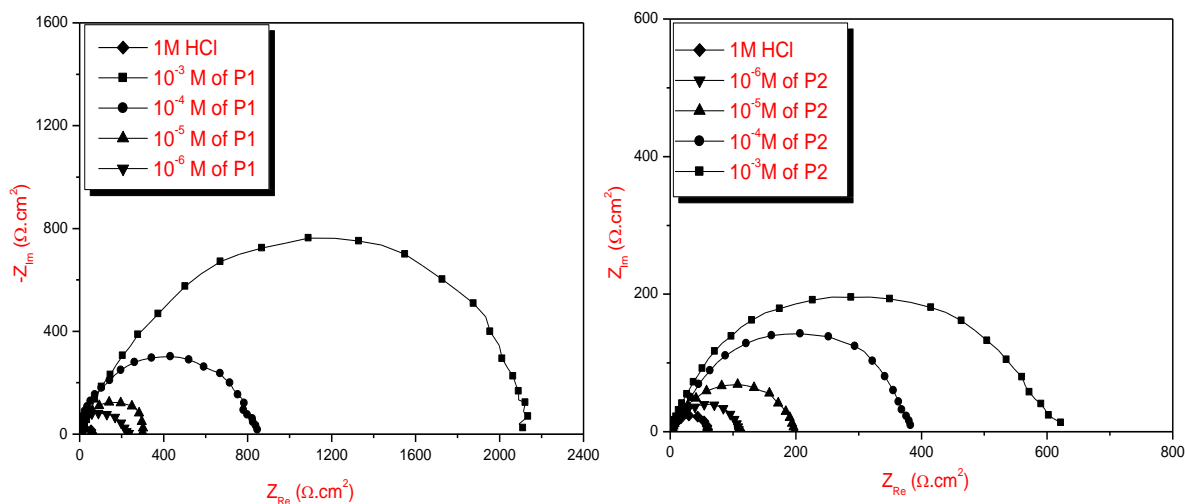
$$E_R \% = \frac{R_{ct}^{-1} - R_{ct(inh)}^{-1}}{R_{ct}^{-1}} \times 100 \tag{4}$$

Where $R_{ct(inh)}$ and R_{ct} are the charge transfer resistance in the presence and absence of different products, respectively.

Results obtained show that R_{ct} increases and C_{dl} tends to decrease with increasing of inhibitor concentration.

A decrease in the C_{dl} values, which can result from a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the inhibitors functions by adsorption at the metal solution/interface [35].

The electrochemical impedance spectroscopy study is good agreement with the result obtained by weight loss and polarization curves measurements.



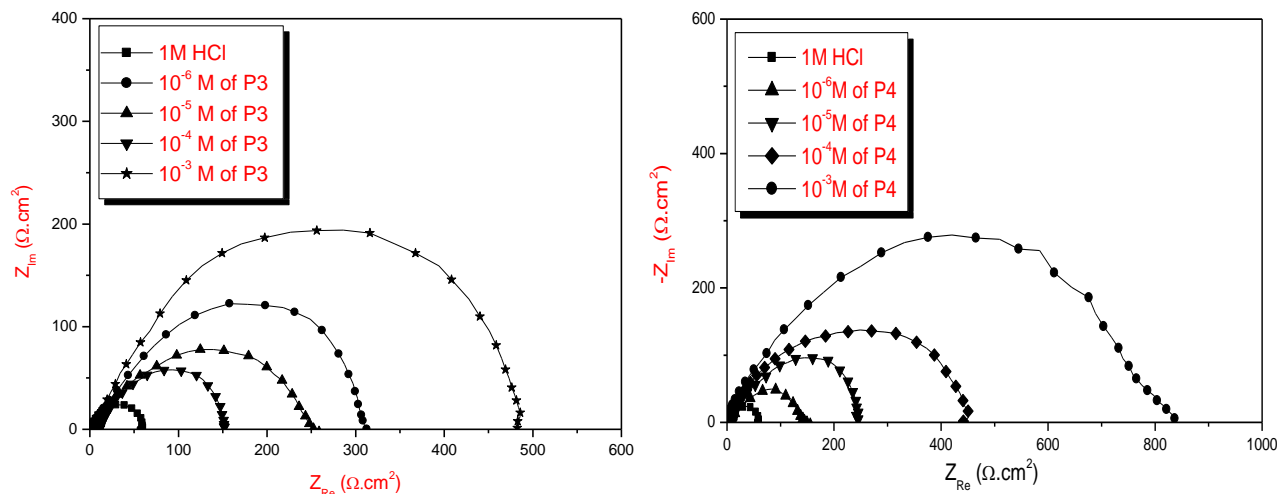


Figure 3. Nyquist diagrams mild steel in 1M HCl without and with different concentrations of inhibitors.

Table 3. Impedance parameters of mild steel in 1M HCl containing different concentrations of pyridazine compounds.

Inhibitors	Concentration (M)	R_{ct} ($\Omega.cm^2$)	F_{max} (Hz)	C_{dl} ($\mu F.cm^{-2}$)	E_R (%)
Blank	1	60	20	133	-
P1	10^{-6}	240	10	66.31	75
	10^{-5}	300	25	21.23	80
	10^{-4}	850	12.5	15	93
	10^{-3}	2150	15.82	4.68	97
P2	10^{-6}	120	31	43	50
	10^{-5}	200	20	39	70
	10^{-4}	400	24	16	85
	10^{-3}	630	25	10	91
P3	10^{-6}	152	10	130	60
	10^{-5}	251	8	80	76
	10^{-4}	353	6	75	81
	10^{-3}	485	10	32	87
P4	10^{-6}	150	15.82	88	60
	10^{-5}	250	7.93	79	76
	10^{-4}	450	6.32	56	87
	10^{-3}	840	15	12	93

4. CONCLUSION

On the basis of these results, the following conclusions may be drawn:

- P1, P3, P3 and P4 inhibit the corrosion of mild steel in 1M HCl. The inhibition efficiency depends on the molecular structure and follows the order: P1 > P2≈P4 > P3.

- The inhibition efficiency increases with increasing inhibitor concentrations to attain a maximum value of 100 % for inhibitor P1 at 10^{-3} M.
- Polarization study shows that pyridazines act as mixed-type inhibitors for an over voltage inferior than -200 mV/SCE.
- Impedance method indicates that pyridazine compounds adsorbs on mild steel surface with increasing charge transfer resistance and decreasing the double-layer capacitance.
- The thio pyridazine compounds are more effective than the corresponding oxo pyridazine compounds. So P1 and P4 are more effective than P2 and P3 respectively.

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