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Comparative Study of new Pyridazine Derivatives Towards Corrosion of Copper in Nitric Acid: Part-1

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The inhibition of the corrosion of copper in 2M HNO_3 by 5-[hydroxy(phenyl)methyl]-6-methylpyridazin-3(2*H*)-one (P1), 4-(2-chlorobenzyl)-6-hydrazino-3-methyl-1,6-dihydropyridazine (P2), 5-(2,6-dichlorobenzyl)-6-methylpyridazin-3(2*H*)-one (P3) and 5-[(2-chlorophenyl)(hydroxy)methyl]-6-methylpyridazin-3(2*H*)-one (P4) has been investigated at 303K using weight loss measurements, potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) methods). Results obtained show that P3 and P4 are the best inhibitors and their inhibition efficiencies (E %) increase with the increase of inhibitor concentration and reach up to 96 and 94 % for P3 and P4 at 10^{-3} M, respectively. Moreover, polarisation studies clearly reveal that the presence of inhibitors changes the mechanism of hydrogen evolution and that they act as mixed inhibitors. EIS study shows that charge transfer resistance increases with the inhibitor concentration. The adsorption of P3 obeys to the Langmuir isotherm. The activation parameters of copper in the presence and absence of P3 are also evaluated and discussed. Effect of temperature is studied between 298 and 353 K and determination of activation parameters is also discussed in part 2. Explanation by quantum indices to correlate inhibition efficiency should be given in part 3.

Keywords: Copper, Nitric acid, Inhibitors, Pyridazines, Polarisation curves, Impedance

1. INTRODUCTION

Corrosion is an electrochemical process by which the metallic structures are destroyed gradually through anodic dissolution [1-3]. Combating corrosion in acidic environment can be achieved by addition of some specific compounds, called inhibitors [4-6]. Heterocyclic organic compounds become more and more accepted as efficient inhibitors in various media. It is admitted that the principal step in the inhibition mechanism is the adsorption of the inhibitor onto the metal surface to form a barrier against the arrival of acidic ions which are responsible on metal dissolution. It has concluded that the inhibitor's adsorption on the metal surface depends mainly on the molecular electronic structure. The adsorption occurs from active centers such as S, N, and O atoms, the double or triple bonds and also aromatic rings. Two modes of adsorption: chemisorption and/or physical adsorption are generally encountered. This phenomenon may be reinforced by the formation of metallic complexes [1–11].

It is assumed that adsorption of organic molecules on metallic surface may be either through vertical or parallel modes and the inhibition process is mainly affected by the inhibitor concentration. For adsorption on iron both vertical and parallel (through л-electrons of aromatic ring) modes are probable, although the vertical is predominant [12-15].

The corrosion inhibition by some pyridazines derivatives has been studied by several researchers [16-20]. 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 of the copper in 2M HNO_3. The study was conducted by gravimetric, potentiokinetic polarization methods and electrochemical impedance spectroscopy (EIS). The chemical structures of the studied pyridazine derivatives are given in Figure 1

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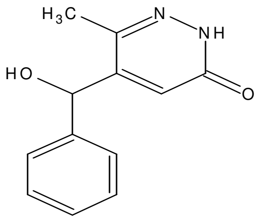
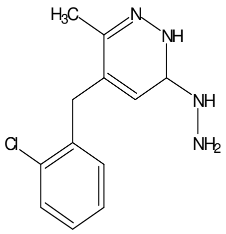
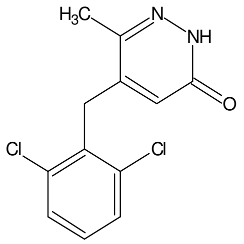
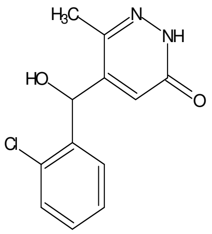
Structure				
name	5-[hydroxy(phenyl) methyl]-6-methylpyridazin-3(2*H*)-one	4-(2-chlorobenzyl)-6-hydrazino-3-methyl-1,6-dihydropyridazine	5-(2,6-dichlorobenzyl)-6-methylpyridazin-3(2*H*)-one	5-[(2-chlorophenyl) (hydroxy)methyl]-6-methylpyridazin-3(2*H*)-one
abbreviation	P1	P2	P3	P4

Figure 1. The proposed structure of the studied pyridazine derivatives.

2. EXPERIMENTAL PART

2.1. Materials and reagents

Copper strips containing 99.5 wt.% Cu, 0.001wt.% Ni, 0.019 wt.% Al, 0.004 wt.% Mn, 0.116 wt.% Si and balance impurities were used for electrochemical and gravimetric studies.

The Copper samples were mechanically polished using different grades of emery paper, washed with double distilled water, and dried at room temperature. Appropriate concentration of aggressive solutions used (2M HNO_3) was prepared using double distilled water. 5-(2-chlorobenzyl)-3-chloro-6-méthylpyridazine, 3-acétyl-4-butanolide, acide 3-(2,6-dichlorobenzyllidène)-lévulinique, hydrate hydrazine, petroleum ether , ethanol , Pyrex tube which, Maxidigest MX 350 Prolabo microwave monomode reactor.

2.2. Synthesis

The product **(P2)** was prepared from *0.01 Mole of 5-(2-chlorobenzyl)-3-chloro-6-méthylpyridazine(I)* in situ by the solid-liquid PTC conditions without solvent [21]. To pyridazin **(I)** (1.2 g, 5 mmol) was added 30 ml of hydrate hydrazine. 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 precipitin formed was filtered and laved with petroleum ether, yield: 96 % of **(P2)** solid.

RMN 1H DMSO : 2.55(s, 3H, CH3); 3.95(s,2H,CH2) ; 6.50(s,1H,H4) ; 4.50(m, 3H,NH); 7.3(m,4H,Hph).

IR (cm-1):3150 (NH); 1650(C=N); 1610, 1500, 1470, 1430 (C=C). Elementary analysis is also made: calculated data: C : 57.9 H5.23 ; N : 22.5 ; Cl : 14.3; found: C : 58.3 ; H : 5.2 ; N : 22.5 ; Cl : 13.9.

P4 ; P1 *:*

The products **(P4, P1)** were prepared from 0.01 Mole of de 3-acétyl-4-butanolide (I) by the solid-liquid PTC conditions [22]. To acetyl **(I)** (0.01 mole) was added in the minimum of ethanol 0.01 mole of hydrate hydrazine. The mixture was refluxed four hours; the mixture was cooled to ambient temperature. The precipitin formed was filtered and recristalised with ethanol, yield: 90 % of corresponding **(P4, P1)** 85%, 90% solids.

P1:

RMN 1H DMSO : 1.60(s, 3H, CH3); 2.35(m,2H,H4) 3.3(m,1H,H5), 4.75(m,1H,CH2); 5.60(d,1H,OH); 10.15(1H, NH); 7.20(m,5H,Hph). IR (cm-1):3400(OH); 3100(NH); 1680(C=O); 1630(C=N); 1450, (C=C aromatique).

P4:

RMN 1H DMSO : 1.75(s, 3H, CH3); 2.20(m,2H,H4) 2.60(m,1H,H5), 4.85 (m,1H,CH2); 5.85(d,1H,OH); 10.35(1H, NH); 7.30(m,5H,Hph). IR (cm-1): 3280(OH); 3280(NH); 1670 (C=O); 1640(C=N); 159-1570, (C=C aromatique).

The product **(P3)** was prepared from 0.01mole of acide 3-(2,6-dichlorobenzyllidène)-lévulinique (I) by the solid-liquid PTC conditions [22]. To acetyl **(I)** (0.01 mole) was added in the minimum of ethanol 0.01 mole of hydrate hydrazine. The mixture was refluxed four hours; the mixture was cooled to ambient temperature. The precipitin formed was filtered and recrystallised with ethanol, yield: 90 % of corresponding **(P3)** 80% solids. RMN 1H DMSO : 2.40(s, 3H, CH3) ;4.10(m,2H,H4) ;5.70(m,1H,H5) ; 7.50(m,3H,Hph), 12.65(1H, NH); IR (cm-1): 3200(NH); 1661 (C=O); 1640(C=N); 1560,1540,1430 (C=C aromatique).

2.3. Measurements

2.3.1. Weight loss measurements.

Gravimetric experiments were carried out in a double walled glass cell. The solution volume was 50 cm^3; the temperature of 303 K was controlled thermostatically. The weight loss of copper in 2M HNO3 with and without the addition of inhibitor was determined after immersion in acid for 1h. The copper specimens were rectangular in the form (2 cm×2 cm × 0.20 cm).

2.3.2. Electrochemical measurements

A three electrode electrochemical cell was used. The working electrode was copper with the surface area of 0.28 cm^2. Before each experiment, the electrode was polished using emery paper until 2000 grade. After this, the electrode was cleaned ultrasonically with distillate water. All potentials were given with reference to the saturated calomel electrode (SCE). The counter electrode was a platinum plate of surface area of 1 cm^2.

The aggressive medium used here is HNO_3 solution. The organic compound tested is pyridazines derivative. Its molecule formula is shown in Fig. 1. The concentration range of this compounds was 10^{-6} to 10^{-3} M.

The working electrode was immersed in test solution during 30 minutes until a steady state open circuit potential (E_{ocp}) was obtained. The polarization curve was recorded by polarization from -150 mV to 150 mV under potentiodynamic conditions corresponding to 1 mV/s (sweep rate) and under air atmosphere. The potentiodynamic measurements were carried out using Tacussel Radiometer PGZ 301, which was controlled by a personal computer.

The electrochemical impedance spectroscopy measurements were carried out using a transfer function analyser (Tacussel Radiometer PGZ 301), with a small amplitude ac. Signal (10 mV rms), over a frequency domain from 100 KHz to 10 mHz at 30°C and an air atmosphere. The polarization resistance R_p, is obtained from the diameter of the semicircle in Nyquist representation.

3. RESULTS AND DISCUSSION

3.1. Gravimetric measurements

The effect of addition of P1, P2, P3 and P4 at different concentrations on the corrosion of copper in 2M HNO_3 solution was studied by weight loss at 1 h. Table 1 gathers the values deduced of W_{corr} and the inhibition efficiency (E%) determined by the equation 1:

$$E_w\% = \frac{(W^0_{corr} - W_{corr})}{W^0_{corr}} \times 100 \tag{1}$$

where W_{corr} and W^o_{corr} are the corrosion rates of copper with and without inhibitor, respectively.

Table 1 indicates clearly a decrease in the corrosion rate in the presence of P1, P2, P3 and P4. This effect is hugely marked at higher concentration of inhibitors. The inhibitive action is more explicit by E% data which increases with inhibitor concentration to reach 93.2% for P1, 83.6% for P2, 96.2% for P3 and 94.3% for P4 at 10^{-3}M. Then all inhibitors studied inhibit the corrosion of copper in 2M HNO_3, but the inhibitor P3 is found to exhibit the best inhibitory action.

Table 1. Gravimetric results of copper in 2M HNO_3 without and with addition of inhibitors at 303 K.

Conc(M)	P1		P2		P3		P4	
	W(mg/cm^2.h)	Ew (%)	W(mg/cm^2.h)	Ew (%)	W(mg/cm^2.h)	Ew (%)	W(mg/cm^2.h)	Ew(%)
Blank	1.78	-	1.78	-	1.78	-	1.78	-
10^{-3}	0.12	**93.2**	0.29	**83.6**	0.07	**96.2**	0.10	**94.3**
$5x10^{-4}$	0.13	92.8	0.30	83.4	0.13	92.6	0.31	82.5
10^{-4}	0.21	88.1	0.51	71.2	0.17	90.1	0.72	59.4
$5x10^{-5}$	0.43	75.8	0.86	51.5	0.62	65.3	1.07	39.7
10^{-5}	0.66	63.0	1.06	40.2	1.27	28.6	1.55	12.6
10^{-6}	1.21	31.9	1.38	22.6	1.53	13.8	1.74	02.0

3.2. Polarization curves

Anodic and cathodic polarization curves for copper in 2M HNO_3 with and without various concentrations of used inhibitors are shown in Figures 2–5.

Various corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}) and the inhibition efficiency (E%) were determined by Tafel extrapolation method and are given in Table 2. E% was calculated using the equation 2:

$$E\% = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \times 100 \qquad (2)$$

where I_{corr} and $I_{corr\ (inh)}$ are the corrosion current density values without and with the inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential.

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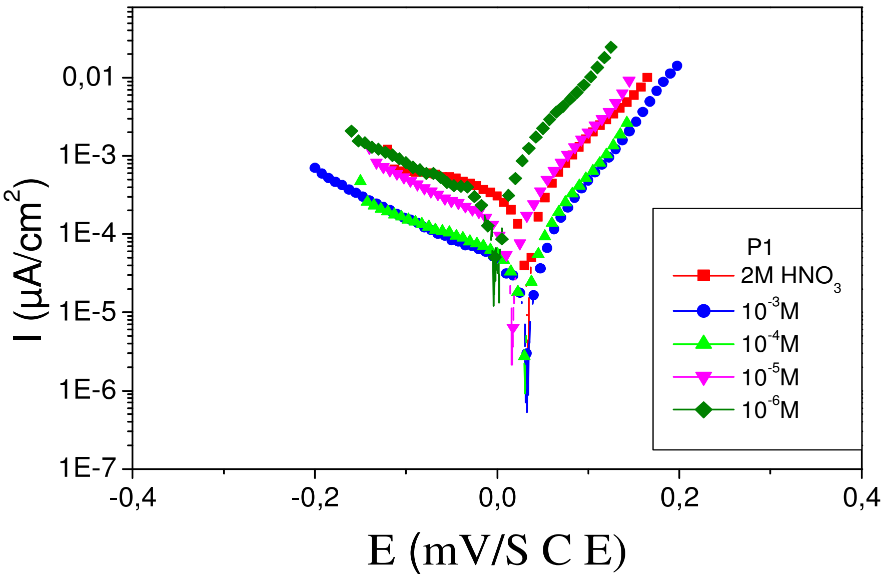

Figure 2. Polarisation curves for Copper in 2M HNO_3 containing different concentrations of P1

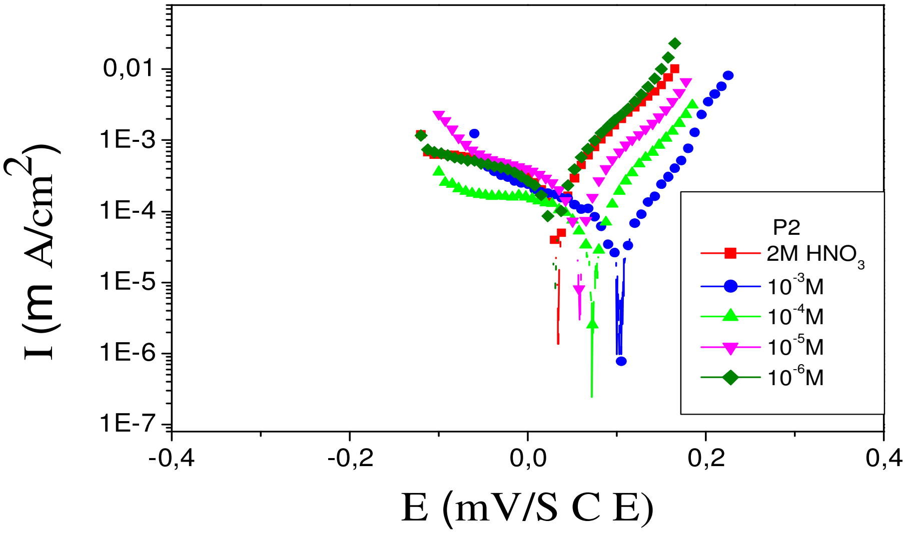

Figure 3. Polarisation curves for Copper in 2M HNO_3 containing different concentrations of P2

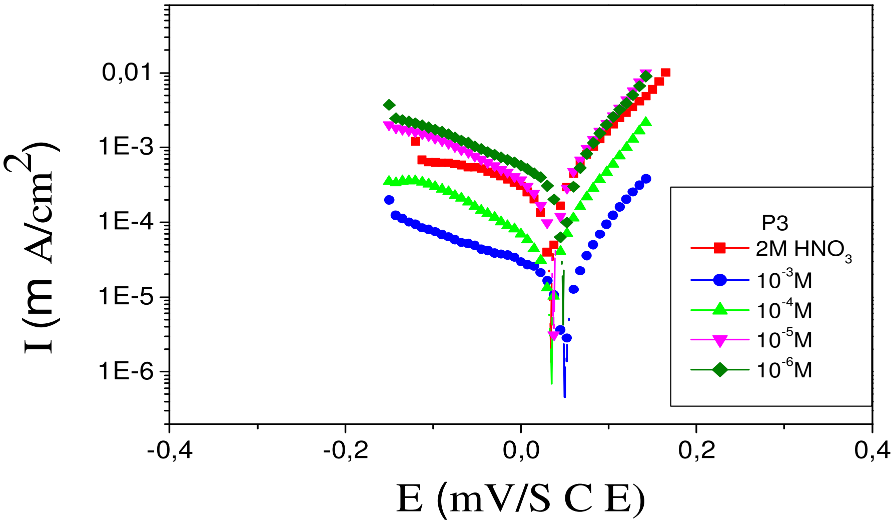

Figure 4. Polarisation curves for Copper in 2M HNO_3 containing different concentrations of P3

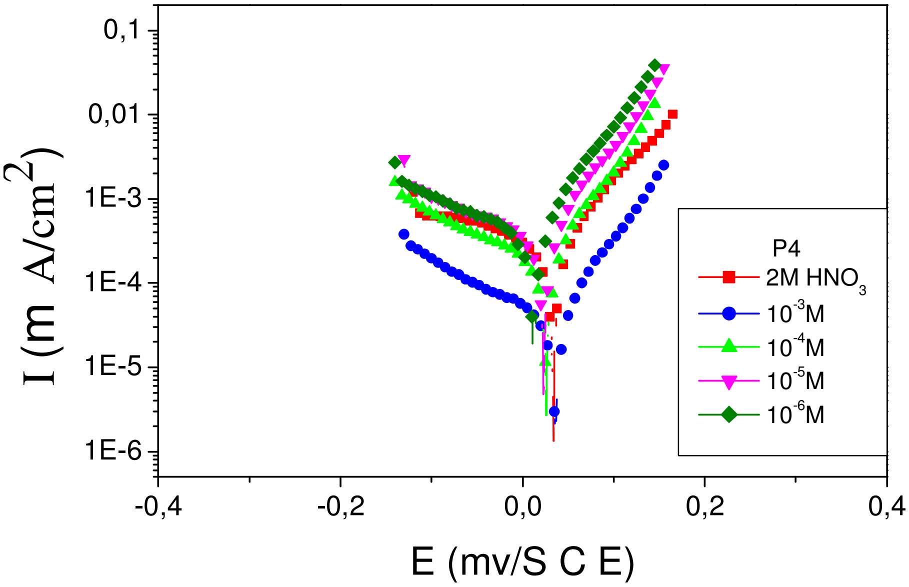

Figure 5. Polarisation curves for Copper in 2M HNO_3 containing different concentrations of P4

It is seen that the addition of various inhibitors affects the polarisation curves and consequently decreases I_{corr} significantly for all the studied concentrations, due to increase in the blocked fraction of the electrode surface by adsorption. The cathodic current versus potential curves gave rise to Tafel lines indicating that the hydrogen evolution reaction is activation-controlled, b_c values is quietly modified and then the addition of inhibitors modifies the mechanism of the proton discharge reaction. In the anodic domain, the presence of these inhibitors hugely decreases anodic current density, the highest effect is observed with P3 and corresponding E% attains 94.3% at 10^{-3}M; the inhibitors act then as mixed inhibitors. In other words, the decrease of corrosion rate observed by gravimetric method may be interpreted by the simultaneous action on cathodic and anodic sites. E_{corr} is modified in the presence of P1 and P2, but in the presence of P3 and P4, no significance effect is observed. This later may be explained by the equal action of P3 on both cathodic and anodic domains

Table 2. Polarisation data of Copper in 2M HNO_3 without and with addition of inhibitors at 303 K.

	Conc (M)	Ecorr (mV/SCE)	$-b_c$ (mV/dec)	I_{corr} ($\mu A/cm^2$)	IE (%)
HNO_3	2	34.00	304.71	365.10	-
P1	10^{-3}	31.80	200.02	038.43	**89.47**
	10^{-4}	29.20	240.68	048.30	86.77
	10^{-5}	15.80	121.94	123.55	66.16
	10^{-6}	-00.20	043.27	248.45	31.95
P2	10^{-3}	102.50	206.08	078.35	**78.54**
	10^{-4}	71.70	397.03	097.28	73.35
	10^{-5}	57.30	263.84	228.67	37.37
	10^{-6}	29.10	309.74	277.69	23.94
P3	10^{-3}	38.90	256.50	020.84	**94.3**
	10^{-4}	33.40	161.30	048.07	86.33
	10^{-5}	36.10	180.97	262.63	28.07
	10^{-6}	47.30	195.26	318.84	12.67
P4	10^{-3}	35.00	193.70	038.10	**89.56**
	10^{-4}	25.00	209.43	157.52	56.85
	10^{-5}	22.50	219.00	310.00	15.09
	10^{-6}	11.40	219.06	336.74	07.77

3.3. Electrochemical impedance spectroscopic studies

Figure 6 presents the Nyquist diagrams obtained in the absence and presence of P3 at different concentrations. The impedance parameters calculated are given in Table 3. The charge-transfer resistance values (R_{ct}) were calculated from the difference in impedance at lower and higher frequencies as suggested by Tsuru et al. [23]. To obtain the double-layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum (–Zimax) is found and C_{dl} values were obtained from the equation 3:

$$f(-Zi\max) = \frac{1}{2\pi C_{dl} R_t} \quad (3)$$

In this case, the inhibition efficiency is calculated using charge transfer resistance from equation 4 [24]:

$$E_Z\% = \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \times 100 \quad (4)$$

where $R_{t(inh)}$ and R_t are the charge transfer resistance in the presence and absence of P3, respectively.

Results obtained show that R_t increases and C_{dl} tends to decrease when the concentration of inhibitor increases. 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 P3 function by adsorption at the metal solution/interface [24].

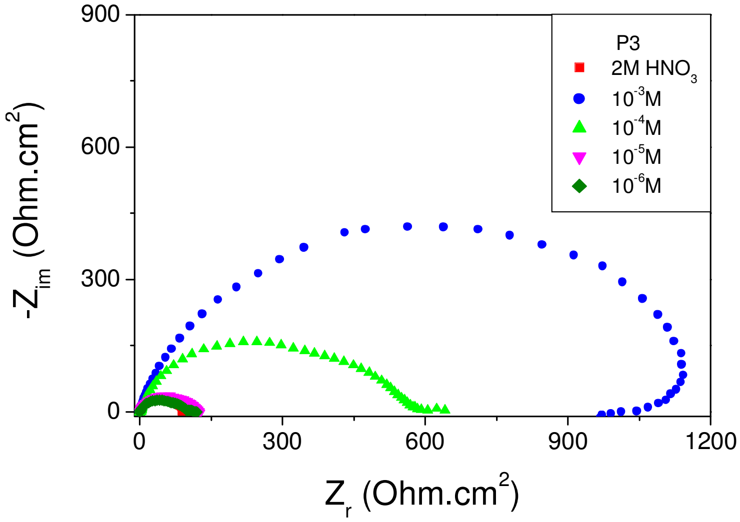

Figure 6. Nyquist diagrams Copper in 2M HNO_3 without and with different concentrations of P3

Table 3. EIS parameters for the Copper corrosion in 2M HNO_3 containing different concentrations of P3.

	Conc (M)	R_t (Ω.cm^2)	f_{max} (Hz)	C_{dl} (μF/cm^2)	ER_t (%)
HNO_3	2	091.41	15.82	110.11	-
P3	10^{-3}	1165.84	02.00	34.11	92.16
	10^{-4}	581.18	05.61	48.77	84.27
	10^{-5}	126.07	07.93	80.70	27.50
	10^{-6}	102.06	15.82	98.60	10.44

4. CONCLUSIONS

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

- P1, P3, P3 and P4 inhibit the corrosion of copper in 2M HNO_3. P3 is found to be more effective.
- The inhibition efficiency increases with increasing of inhibitor concentration to attain a maximum value of 96 % for inhibitor P3 at 10^{-3} M.
- Polarisation study shows that pyridazines act as mixed-type inhibitors.

- Impedance method indicates that P3 adsorbs on the copper surface with increasing transfer resistance and decreasing of the double-layer capacitance.

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References

1. V.S. Sastri, Corrosion Inhibitors, Principles and Applications, John Wiley & Sons, New York, 1998, p. 25 and 237.
2. M. M. Antonijevic, M. B. Petrovic, *Int. J. Electrochem. Sci.*, 3 (2008) 1.
3. A. Chetouani, A. Aouniti, B. Hammouti, N. Benchat, T. Benhadda, S. Kertit, *Corros. Sci.* 45 (2003) 1675.
4. I.N. Putilova, S.A. Balezin, V.P. Barannik, Metallic Corrosion Inhibitors, Pergamon Press, Oxford, 1960,
5. A. Chetouani, K. Medjahed, K.E. Sid-Lakhdar, B. Hammouti, M. Benkaddour, A. Mansri, *Corros. Sci.* 46 (2004) 2430.
6. A.P. Srikanth, T.G. Sunitha, V. Raman, S. Nanjundan, N. Rajendran, *Mater. Chem. Phys.* 103 (2007) 241.
7. A. Zarrouk, A Dafali, B. Hammouti, H. Zarrok, S. Boukhris, M. Zertoubi, *Int. J. Electrochem. Sci.*, 5 (2010) 46.
8. K.F. Khaled, S.A. Fadl-Allah, B. Hammouti, *Mater. Chem. Phys.* 117 (2009) 148.
9. A. Abdallah, M. Al- Agez, A.S. Fonda, *Int. J. Electrochem. Sci.,* 4 (2009) 336.
10. M. El Achouri, M.R. Infante, F. Izquierdo, S. Kertit, H.M. Gouttaya, B. Nciri, *Corros. Sci.* 43 (2001) 19.
11. V. Shinde, A.B. Gaikwad, P.P. Patil, *Appl. Surf. Sci.* 253 (2006) 1037.
12. M.R. Arshadi, M. Lashgari, Gh.A. Parsafar, *Materials Chemistry and Physics* 86 (2004) 311-314.
13. B. Hammouti, A. Aouniti, S. Kertit, M. Brighli, *Corrosion,* 51 (1995) 194.
14. M. Lashgari, M.R. Arshadi, Gh.A. Parsafar, *Corrosion,* 61 (2005) 778.
15. A. O. James, N. C. Oforka, Olusegun K. Abiola, *Int. J. Electrochem. Sci.,* 2 (2007) 278.
16. F. Bentiss, F. Gassama, D. Barbry, L. Gengembre, H. Vezin, M. Lagrenée, M. Traisnel, *Appl. Surf. Sci.* 252 (2006) 2684.
17. A. Chetouani, B. Hammouti, A. Aouniti, N. Benchat, T. Benhadda, *Prog. Org. Coat.* 45 (2003) 73.
18. A. Chetouani, A. Aouniti, B. Hammouti, N. Benchat, T. Benhadda, S. Kertit, *Corros. Sci.* 45 (2003) 1675.
19. M. Bouklah, N. Benchat, A. Aouniti, B. Hammouti, M. Benkaddour, M. Lagrenée, H. Vezin, F. Bentiss, *Prog. Org. Coat.* 51 (2004) 118.
20. M. Bouklah, N. Benchat, B. Hammouti, A. Aouniti, S. Kertit, *Materials Letters* 60 (2006) 1901.
21. C.O. Kappe, D. Dallinger, *Nat. Rev. Drug. Discov.* 5 (2006) 51.
22. C.G. Rubat, P. Coudert, J. Couquelet, P. Bastide, J. Bastide, *Chem. Pharm. Bull. 36* (1988) 1558.
23. T. Tsuru, S. Haruyama, B. Gijutsu, *J. Jpn. Soc. Corros. Eng.* 27 (1978) 573.
24. E. McCafferty, N. Hackerman, *J. Electrochem. Soc.* 119 (1972) 146.