

Experimental and quantum chemical studies on the corrosion inhibition effect of synthesized pyrazole derivatives on mild steel in hydrochloric acid

H. B. Ouici¹ · O. Benali² · A. Guendouzi¹

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Two heterocyclic compounds of the pyrazole family were synthesized by Abstract cyclocondensation reaction of chalcone derivatives with thiosemicarbazide. The structures of the synthesized pyrazoles, namely, 3,5-diphenyl-4,5-dihydro-1H-pyrazole-1carbothioamide (DPC) and 5-(3-methoxyphenyl)-3-phenyl-4,5 dihydro-1H-pyrazole-1carbothioamide (DPCM), were confirmed by infrared IR, ¹H NMR and ¹³C NMR spectra. The surface activity of these compounds showed their tendency towards adsorption at the interfaces. The prepared compounds were evaluated as corrosion inhibitors for mild steel in 1 M HCl solution using the gravimetric method. These measurements indicate that the inhibition efficiency of the pyrazole derivatives increased with concentration inhibitor, whereas the latter decreased with temperature. The adsorption of the inhibitors on the mild steel surface obeyed the Langmuir adsorption isotherm, and the calculated ΔG_{ads}^0 values of the synthesized inhibitors suggested that the adsorption of these compounds involves two types of interaction, chemisorption and physisorption. The results of the corrosion inhibition using two different heterocyclic compounds showed that the DPCM is more effective than the PCM in 1 M HCl medium.

Keywords Corrosion · Inhibitor · Pyrazole · Mild steel

Introduction

Mild steel is widely used in a variety of industrial applications such as the petroleum industries. It has also become the metal of choice for pipelines, power plants, etc. [1-4]. Hydrochloric acid solutions are widely used for pickling, descaling, acid

H. B. Ouici ouicihouari@hotmail.fr

¹ Department of Chemistry, Faculty of Science, University of Saida, 138 Saida, Algeria

² Department of Biology, Faculty of Science, University of Saida, 138 PB Saida, Algeria

cleaning, oil well acidizing, etc. [5]. The use of an inhibitor is very effective in reducing the rate of dissolution of metals [6]. The organic compounds are known to be applicable as corrosion inhibitors for steel in acidic environments [7-14]. Such compounds typically contain nitrogen, oxygen or sulfur heteroatoms in a conjugated system and function via adsorption of the molecules on the metal surface, creating a barrier against corrosion attack [15–19]. The adsorption bond strength depends on the composition of the metal, the inhibitor structure and concentration, and temperature. The corrosion inhibition of steel in acid medium has been reported recently by using hetrocyclic compounds such as triazoles [20–23], thiadiazoles [24, 25], and oxadiazoles [26, 27] derivatives as inhibitors. Generally, corrosion can be prevented by the action of adsorptive inhibitors which prevent the adsorption of the aggressive anions or by the formation of organic layers on the metal surface [23, 28].

Pyrazole compounds have been reported as inhibitors against the corrosion of mild steel [29, 30]. The action of such inhibitors depends on the specific interaction between the functional groups and the metal surface. The presence of the -C-N- group and electronegative nitrogen in the molecules increases their adsorption properties [31]. The adsorption of these molecules depends mainly on certain physicochemical properties such as functional groups, steric factors, aromaticity, electric density at the donor atoms and the *p*-orbital character of donating electrons [32]. The inhibitor adsorption onto the metal surface is either physisorption [33] or chemisorption [34], which depends on the strength and the nature of the bonds formed between the inhibitor molecules and the metal surface. Molecules that contain both nitrogen and sulfur are of particular importance since these provide an excellent inhibition in comparison with the compounds contained either sulfur or nitrogen [35, 36]. In this study, two series of pyrazoles, namely, 3,5-diphenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide (DPC) and 5-(3-methoxyphenyl)-3-phenyl-4,5 dihydro-1H-pyrazole-1-carbothioamide (DPCM) (Fig. 1), were synthesized and evaluated for their inhibition towards mild steel corrosion reactions in 1 M HCl solution at different temperatures. The relationship between the surface activity and the corrosion inhibition efficiency of the synthesized compounds is discussed.





1-carbothioamide (DPC)

Fig. 1 Molecular structure of pyrazoles

3,5-diphenyl-4,5-dihydro-1H-pyrazole- 5-(3-methoxyphenyl)-3-phenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide (DPCM)

Experimental

Chemistry

The reaction sequences employed for synthesis of the target pyrazole derivatives are illustrated in Schemes 1 and 2.

In the present work, two types of pyrazole were prepared utilizing the cyclocondensation reaction between chalcones derivatives and thiosemicarbazide. In basic media, the key chalcone intermediates (**3a**, **b**) were synthesized through the Claisen–Schmidt condensation of equimolar amounts of acetophenone (**1**) and benzaldehyde derivatives (**2a**, **b**) through stirring the reactants in aqueous alcoholic solution containing 20 % sodium hydroxide at room temperature for 24 h in accordance with the method described in the literature (Scheme 1) [37–39]. The newly synthesized compounds, 3,5-disubstitued pyrazolecarbothioamides (**5a**, **b**), were obtained by heating reflux equimolar amounts of thiosemicarbazide (**4**) and the corresponding unsaturated ketones (**3a–b**) in hot ethanolic sodium hydroxide solution for 8 h (Scheme 2) [40]. These pyrazole derivatives (**5a**, **b**) were characterized using IR and NMR spectra. IR spectra showed strong absorption bands at 3479.08 and 3344.21 cm⁻¹ due to the primary amine group (–NH₂). Furthermore, ¹³C NMR spectra displayed a signal at 176.55–176.90 ppm assignable to thiocarbamovl carbon (C=S).

✓ Synthesis of chalcones



Scheme 1 Synthesis of chalcones derivatives

✓ Synthesis of pyrazoles





Further evidence for the formation of the 4,5-dihydropyrazole ring was obtained from ¹H and ¹³C NMR spectra which provide diagnostic tools for the positional elucidation of the protons. The geminal pyrazoline protons at $(C2-H_a)$ appeared in the region of 3.10–3.36 ppm and 3.85–3.95 ppm as a doublet of doublets in all compounds. The (H_b) proton at C3 also appears as a doublet of doublets in the region of 5.90–5.95 ppm due to vicinal coupling with two nonmagnetically equivalent geminal protons of C2 carbon. The signals obtained from the ¹³C NMR spectra further confirmed the proposed structures; the C2 and C3 carbons of the pyrazoline ring resonated at 42.85–42.81 and 63.30–63.22 ppm, respectively. All compounds showed signals at 176.57–176.61 ppm, which was assignable to thione carbon (C=S) of the pyrazoline ring. It should be noted that the ¹³C NMR spectrum of pyrazole **5b** showed a characteristic signal at 55.42 matching the carbon of the methoxy (–OCH₃) group.

All the target compounds were characterized by using thin layer chromatography and melting point techniques. Both analytical and spectral data of all the compounds are in full agreement with the proposed structures. Moreover, comparison of the spectroscopic data of the new compounds with those of the previously reported analogues further confirmed the above structures [40]. These compounds were used in the this work as a corrosion inhibitor of mild steel in 1 M HCl medium.

General

Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected. IR spectra (KBr, cm⁻¹) were recorded on Bruker or Testscan Shimadzu FT 8000 spectrometers. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AC 200 and Avance 300 MHz spectrometers, respectively, in DMSO-d6 as a solvent and tetramethylsilane (TMS) as an internal standard (chemical shift in *d*, ppm). TLC was performed on silica gel G (Fluka) and spots were visualized by iodine vapors or irradiation with UV light (254 nm). All the chemicals were purchased from Sigma–Aldrich. The chalcone intermediates (**3a**, **b**) were synthesized in accordance with the method described in the literature [37–39]. Pyrazole (**5a**, **b**) derivatives were prepared according to the reported method [40].

General procedure for the preparation of chalcone analogues 3a-b

Chalcone analogues were prepared by condensation of acetophenone (1) and aldehyde derivatives (**2a**, **b**) in ethanol solution, applying 20 % aqueous NaOHas a catalyst. To a stirred solution of 6.17 g of acetophenone (0.051 mol) and aldehydes (0.051 mmol) in ethanol (15 ml); an aqueous solution of 20 % NaOH was added. The resulting solution was heated to 60 °C for 1 h and then allowed to stand overnight at room temperature with continuous stirring. The reaction mixture was poured into cold water and precipitate was collected by filtration, washed with 50 % ethanol, dried, and recrystallized from ethanol to give **3a**, **b** in good yields.



Fig. 2 IR spectra of (E)-1,3-diphénylprop-2-éne-1-one (3a)



Fig. 3 ¹H NMR spectra of (E)-1,3-diphénylprop-2-éne-1-one (3a)

(*E*)-1,3-diphénylprop-2-éne-1-one (**3a**) Yield: 85 %; m.p. 55 °C; crystallized from ethanol. *IR* (cm⁻¹): 3055.77–3027.94 (C–H, aromatic), 1661.51 (C=O, carbonyle), 1573.79 (C=C, oléfine) Fig. 2. ¹H RMN (DMSO- d_6 , 300 MHz, δ (ppm)): 8.18 (d, 2H, H_a), 7.99 (d, 1H, H_b), 7.58 (d, 1H, H_c), 7.45–7.65 (m, 8H, H_d) Fig. 3.

¹³*C RMN* (*DMSO-d*₆, 300 MHz, δ (ppm)): 189.67 (C₁), 122.51 (C₂), 144.51 (C₃), 138.01 (C₄'), 135.11 (C₄), 133.64 (C₇), 131.12 (C_{7'}), 128.61–129.27 (C₅, C₆, C₈ et C₉), 128.11–128.38 (C_{5'}, C_{6'}, C_{8'} et C_{9'}) Fig. 4.

(*E*)- 3-(3-methoxyphenyl)-1-phenylprop-2-en-1-one (**3b**) Yield: 70 %; m.p: 60 °C; crystallized from ethanol; *IR* (Cm⁻¹):3050.13 (C–H, aromatique), 2955.15–2831.66 (C–H, OCH₃), 1655.35 (C=O, carbonyle), 1572.94 (C=C, oléfine), 1259.81 (C–O, OCH₃) Fig. 5, ^{*I*}*H RMN* (*DMSO-d*₆, 300 MHz, δ (ppm)): 8.17 (d, 2H, H_a), 7.94 (d, 1H, H_b), 7.59 (d, 1H, H_c), 7.03–7.67 (m, 8H, H_d), 3.83 (s, 3H, –OCH₃) Fig. 6, ^{*I*3}*C RMN* (*DMSO-d*₆, 300 MHz, δ (ppm)): 189.68 (C₁), 122.76 (C₂), 144.51 (C₃), 160.11 (C₆) 137.98 (C_{4'}), 136.52 (C₄), 133.66 (C_{7'}), 113.83 (C₅), 117.23 (C₇), 55.77 (C₁₀) Fig. 7.

General procedure for synthesis of pyrazole compounds 5a-b

A suspension of chalcones (0.014 mol), sodium hydroxide (0.035 mol) in ethanol (95 %) (30 mL) and thiosemicarbazide (0.014 mol) was added. The mixture was refluxed for 8 h. The products were poured into crushed ice and the solid mass which separated out was filtered, dried and crystallized from ethanol (95 %).

3,5-diphenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide (**5a**) Yield: 57 %; m.p: 202 °C; crystallized from ethanol; *IR* (cm⁻¹): 3479.08–3344.21 (NH₂), 3053.44 (C–H, aromatic), 1599.20 (C=C, aromatic) Fig. 8. ¹H RMN (DMSO-d₆, 300 MHz, δ (ppm)): 3.10–3.36 (dd, 1H, C2–H_a of pyrazole), 3.85–3.95 (dd, 1H, C2–H_a of pyrazole), 5.90–5.95 (dd, 1H, C3–H_b of pyrazole), 7.11–8.084 (m, 10H, ArH+ s, 2H, NH₂) Fig. 9. ¹³C RMN (DMSO-d₆, 300 MHz, δ (ppm)): 176.57 (C₁₀), 155.39 (C₁), 143.46 (C₄), 131.35 (C_{4'}), 125.74–131.02 (C₅–C₉ et C_{5'}–C_{9'}), 63.30 (C₃), 42.85 (C₂) Fig. 10.

5-(3-methoxyphenyl)-3-phenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide (5b) Yield: 67 %; m.p: 190 °C; crystallized from ethanol; IR (Cm⁻¹):3428.44–3253.59 (NH₂), 3140–3055.01 (C–H, aromatic), 2999.70–2832.85 (C–H, –OCH₃), 1576.08 (C=C, aromatic) Fig. 11. ¹H RMN (DMSO-d₆, 300 MHz, δ (ppm)): 3.10–3.36 (dd, 1H, C2–H_a of pyrazole), 3.82–3.93 (dd, 1H, C2–H_a of pyrazole+ s, 3H, OCH₃), 5.87–5.92 (dd, 1H, C3–H_b of pyrazole), 7.11–7.89 (m, 10H, ArH+ s, 2H, NH₂) Fig. 12. ¹³C RMN (DMSO-d₆, 300 MHz, δ (ppm)): 176.61 (C₁₀), 159.79 (C₆), 155.44 (C₁), 145.04 (C₄), 131.34 (C_{4'}), 127.57–131.03 (C₈–C₉ et C_{5'}–C_{9'}), 111.84–112.30 (C₅ et C₇), 63.22 (C₃), 55.42 (C₁₁), 42.81 (C₂) Fig. 13.

Surface activity of pyrazole derivatives

Material

Tests were performed on a freshly prepared sheet of mild steel of the following composition (wt%): 0.1 % C, 0.03 % Si, 0.2 % Mn, 0.02 % P, 0.05 % Cr, 0.05 % Ni, 0.03 % Al, and balance Fe. Specimens used in the weight loss



Fig. 4 ¹³C NMR spectra of (E)-1,3-diphénylprop-2-éne-1-one (3a)



Fig. 5 IR spectra of (E)-3-(3-methoxyphenyl)-1-phenylprop-2-en-1-one (3b)



Fig. 6 ¹H NMR spectra of (E)-3-(3-methoxyphenyl)-1-phenylprop-2-en-1-one (3b)



Fig. 7 13 C NMR spectra of (E)-3-(3-methoxyphenyl)-1-phenylprop-2-en-1-one (3b)

experiment were mechanically cut into $13.35 \times 10.25 \times 2.85$ mm dimensions, and then abraded with SiC abrasive papers 320, 400, 600, 800 and 1000 grit, respectively, washed in absolute ethanol or acetone, dried at room temperature and stored in a moisture-free desiccator before their use in the corrosion studies.

Solutions

An aggressive solution, 1 M HCl, was prepared by dilution of analytical grade 37 % HCl with distilled water. This solution was used for all experimental purposes. The concentration range of DPC and DPCM prepared and used in this study was 4×10^{-4} to 10^{-3} M.

Gravimetric measurements

The gravimetric method (weight loss) is probably the most widely used method of inhibition assessment. The simplicity and reliability of the measurement offered by the weight loss method is such that the technique forms the baseline method of measurement in many corrosion monitoring programmes. Weight loss measurements were conducted under total immersion using 250-mL beakers containing 200 DPC and DPCM test solutions at 303–313 K maintained in a thermostated water bath. The mild steel coupons were weighed and suspended in the beaker with the help of a rod and hook. The coupons were retrieved after 1 h immersion, washed in distilled water, dried in acetone, and re-



Fig. 8 IR spectra of 3,5-diphenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide (5a)



Fig. 9 ¹H RMN spectra of 3,5-diphenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide (5a)



Fig. 10 ¹³C RMN spectra of 3,5-diphenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide (5a)



Fig. 11 IR spectra of 5-(3-methoxyphenyl)-3-phenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide



Fig. 12 ¹H spectra of 5-(3-methoxyphenyl)-3-phenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide



Fig. 13 ¹³C spectra of 5-(3-methoxyphenyl)-3-phenyl-4,5-dihydro-1H-pyrazole-1-carbothioamide

weighed. The weight loss, in grams, was taken as the difference in the weight of the mild steel coupons before and after immersion in different concentrations of the DPC and DPCM solutions. Then, the tests were repeated at different temperatures. In order to get good reproducibility, experiments were carried out in triplicate. In this present study, the standard deviation values among parallel triplicate experiments were found to be smaller than 2 %, indicating good reproducibility.

The corrosion rate (W) in mg/cm^2 h was calculated from the following equation [41]:

$$v = \frac{\Delta w}{S \times t} \tag{1}$$

where Δw is the average weight loss of three mild steel sheets, *S* the total area of one mild steel specimen, and *t* is the immersion time (1 h). With the calculated corrosion rate, the inhibition efficiency (%IE) was calculated as follows:

$$IE\% = \frac{v_0 - v}{v_0} \times 100$$
 (2)

where v_0 and v are the corrosion rates of the mild steel coupons in the absence and presence of the inhibitor, respectively.

Results and discussion

Gravimetric studies

Effect of DPC and DPCM concentration and temperature on inhibition efficiency

The electrochemical theory of corrosion proposed that corrosion of metals is largely accompanied by the action of a network of short-circuited electrolytic cells on the metal surfaces [42]. Iron (II) ions go into solution at the anodes of these cells in amounts chemically equivalent to the reaction at the cathodes. The anodic dissolution reaction of iron in hydrochloric acid solution is as follows:

$$Fe \rightarrow Fe^{2+} + 2e$$
 (3)

On the other hand, the reaction at the cathodes which lead to hydrogen evolution can be represented as:

$$2\mathrm{H}^{+} + 2\mathrm{e} \to 2\mathrm{H}_{\mathrm{ads}} \tag{4}$$

$$2H_{ads} \rightarrow H_2$$
 (5)

Thus, reactions (3)–(5) lead to the corrosion of mild steel in a hydrochloric acid solution. It is generally accepted that the first step in the adsorption of an organic inhibitor on a metal surface usually involves the displacement of one or more water molecules adsorbed at the metal surface [43].

$$Inh_{(sol)} + nH_2O \leftrightarrow Inh_{(ads)} + nH_2O_{(sol)}$$
 (6)

where *n* is the size ratio, that is, the number of water molecules replaced by one organic inhibitor. The inhibitor may then combine with freshly generated Fe^{2+} ions on the steel surface (Eq. 3), forming metal–inhibitor complexes:

$$\operatorname{Fe}^{2+} + \operatorname{Inh}_{(ads)} \to [\operatorname{Fe}-\operatorname{Inh}]_{(ads)}$$
 (7)

The resulting complex could, depending on its relative solubility, either inhibit or catalyze further metal dissolution. Weight loss measurements were carried out in 1 M HCl in the absence and presence of different concentrations of DPC and DPCM at 303 and 313 K in order to determine the effectiveness of these compounds as corrosion inhibitors. Figures 14 and 15 show the corrosion rate values of mild steel with different concentrations of DPC and DPCM in 1.0 M HCl solution at 30 and 40 °C. The corrosion rate values decrease as the concentration of the inhibitors increases; this behavior is due to the absorption of inhibitors on the mild steel surface [44]. It should be noted that the corrosion rate strongly decreases in the presence of DPCM at the two temperatures; indeed, the presence of the methoxy ($-OCH_3$) group in the DPCM structure increases the adsorption of this compound on the metal surface. This observation shows the importance of the molecular structure on the inhibitory capacity of the organic compounds used for the inhibition of corrosion.

The values of inhibition efficiency of the investigated compounds are given in (Table 1). From this table, the order of the inhibition efficiency of pyrazole derivatives is as follows: DPCM > DPC. It is obvious that the inhibition efficiency increases with increasing the concentration of pyrazole derivatives [29, 45].



Fig. 14 Relationship between corrosion rate (ν) and concentrations of DPC and DPCM in 1 M HCl at 30 °C



Fig. 15 Relationship between corrosion rate (ν) and concentrations of DPC and DPCM in 1 M HCl at 40 °C

Figures 16 and 17 show the inhibition efficiency of DPC and DPCM at two temperatures, 30 and 40 °C. Globally, the inhibition efficiency obtained from weight loss measurements for different methods has been estimated at about 73 and 68 % and 97 and 99 % at very low concentrations (10^{-3} M) of DPC and DPCM, respectively for T = 30 and 40 °C. These results indicate that DPCM is more effective than DPC for corrosion inhibition of mild steel in 1 M hydrochloric acid.

Inhibitor	Conc. (Mol/L)	303 K		313 K		
		V (mg/cm ² h)	% IE	V (mg/cm ² h)	% IE	
DPC	Blanc	4.2	_	4.70	_	
	4×10^{-4}	1.96	53.00	2.80	40	
	5×10^{-4}	1.55	63.09	2.70	42.60	
	7×10^{-4}	1.42	66.19	2.20	53.20	
	10^{-3}	1.13	73.09	1.15	68.00	
DPCM	4×10^{-4}	0.40	90.47	0.16	96.60	
	5×10^{-4}	0.34	91.90	0.14	97.02	
	7×10^{-4}	0.23	94.52	0.09	98.08	
	10^{-3}	0.12	97.14	0.04	99.14	

 Table 1
 Calculated values of corrosion rate and inhibition efficiency for mild steel corrosion in 1 M HCl

 in the absence and presence of DPC et DPCM



Fig. 16 Variation of inhibition efficiency % IE of DPC and DPCM at 30 °C



Fig. 17 Variation of inhibition efficiency % IE of DPC and DPCM at 40 °C

Adsorption isotherm

The adsorption isotherms describe the behavior of the inhibitor molecules and provide information about the interaction of the inhibitor molecules with the electrode surface [33, 34, 46]. The adsorption of inhibitors at the metal–solution interface is represented as a substitution adsorption process between the inhibitor molecules ($Inh_{(sol)}$) and the water molecules on the metallic surface(H_2O_{ads}):

$$Inh_{(sol)} + nH_2O \leftrightarrow Inh_{(ads)} + nH_2O_{(sol)}$$

where $Inh_{(sol)}$ and $Inh_{(ads)}$ are the inhibitor species dissolved in the aqueous solution and adsorbed onto the metallic surface, respectively. $H_2O_{(ads)}$ is the water molecules adsorbed on the metal surface and *n* is the ratio which represents the number of water molecules replaced by a single inhibitor molecule. Fitting of the gravimetric measurement data describes the mode of interaction occurred between the inhibitor molecules and the metal surface. One of the most famous models used to fit the surfactant systems in the adsorption state is the Langmuir adsorption isotherm [46]. This model considers two interactions: the inhibitor–molecules interaction and the inhibitor–aqueous medium interaction. The correlation between θ and inhibitor concentration C_i in the corrosive medium can be represented by the Langmuir adsorption isotherm according to Eq. (8):

$$\frac{C_{\rm i}}{\theta} = \frac{1}{K_{\rm ads}} + C_{\rm i} \tag{8}$$

where K_{ads} is the equilibrium constant of the inhibitor adsorption process and C_i is the inhibitor concentration. Straight line plots of C_i/θ versus C_i indicate that the



Fig. 18 Langmuir adsorption plot for mild steel in the presence of DPC at 30 and 40 °C



Fig. 19 Langmuir adsorption plot for mild steel in the presence of DPCM at 30 and 40 °C

adsorption of the inhibitor molecules on the metal surface obeyed the Langmuir adsorption model (Figs. 18, 19). The regression coefficients of the fitted curves are around unity (r > 0.985). This reveals that the inhibition tendency of the inhibitors is due to the adsorption of these molecules on the metal surface [47] (Table 2). However, the slopes of the C_i/θ versus C_i plots are close to unity which indicates that the adsorption of pyrazole compounds under consideration on the mild steel/

Table 2Thermodynamicparameters of the adsorption ofDPC and DPCM on mild steelsurfaces in 1 M HCl	Inhibitor	<i>T</i> (K)	Regression coefficient (<i>r</i>)	Slope	<i>K</i> _{ads}	$\Delta G_{ m ads}$ (kJ/mol)
	DPC	303	0.99	1.07	3.33×10^{3}	-30.55
		313	0.99	0.97	1.2×10^4	-36
	DPCM	303	0.99	0.96	1.8×10^4	-34.80
		313	0.99	0.97	5×10^5	-38.60

acidic solution interface follows the Langmuir adsorption isotherm [47, 48]. K_{ads} values were calculated from the intercepts of the straight lines on the C_i/θ axis [49, 50] and correlated to the standard free energy of adsorption (ΔG_{ads}^0) as:

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{\text{ads}}^0}{RT}\right) \tag{9}$$

The value 55.5 in Eq. 9 is the molar concentration of water in solution. The values of K_{ads} and Δ_{ads}^0 of DPC and DPCM inhibitors are listed in Table G2. The negative sign of ΔG_{ads}^0 indicates that the inhibitor molecules are spontaneously adsorbed onto the metal surface [51].

In the present study, the calculated values of ΔG_{ads}^0 ads obtained for DPC and DPCM range between -30.55 and -36 at 30 °C and -34.80 and -38.60 at 40 °C, respectively, indicating that the adsorption of mechanism of DPC and DPCM on mild steel in 1 M HCl solution at the studied temperatures may be a combination of both physisorption and chemisorption (comprehensive adsorption) [52-58]. However, physisorption was the major contributor while chemisorption contributed only slightly to the adsorption mechanism judging from the decrease of %IE with the increase in temperature in the presence of the DPC inhibitor. In the case of DPCM, the chemisorption process is favored because the inhibition efficiency % IE increases with increasing temperature. The high K_{ads} and ΔG_{ads}^0 values may be attributed to higher adsorption of the inhibitor molecules at the metal-solution interface [35, 36]. In the physisorption process, it is assumed that acid anions such as Cl⁻ ions are specifically adsorbed on the metal surface, donating an excess negative charge to the metal surface. In this way, the potential of zero charge becomes less negative which promotes the adsorption of inhibitors in cationic form (Fig. 20) [33, 59] (Scheme 3).

Theoretical calculations

Quantum chemical calculations

To investigate the correlation between the molecular structure of pyrazoles and its inhibition effect, a quantum chemical study has been performed. Geometric structures and electronic properties of DPC and DPCM have been calculated by GAUSSIAN 09W software [60], using the Becke's three-parameter hybrid density functional B3LYP [61] method with the standard 6-31G* basis set. Figure 21 shows



Fig. 20 Physisorption process of pyrazole on mild steel surfaces by the synergistic effect of chloride Cl⁻ ions



Scheme 3 Cationic form of pyrazole derivatives in 1 M HCl medium (protonation)

the optimized molecular structures, highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO), of pyrazoles. It shows that the benzene ring, N and S atoms have larger electric density. It is suggested that the benzene ring, N and S atoms can be suitable places for adsorption onto surfaces, especially in the case of N and S because of their lone pair of electrons. DPC and DPCM molecules can be directly adsorbed at the steel surface on the basis of donor–acceptor interactions between the π -electrons of conjugated systems (benzene and pyrazole ring), heteroatoms (S, N and O), and the vacant *d*-orbitals of iron atoms.

Thus, we suggest that the electron pair of the nitrogen and sulfur atoms is able to make a complex with vacant *d*-orbitals of Fe^{2+} (Scheme 4).

The HOMO and LUMO energies, the LUMO–HOMO energy gap the dipole moment and the volume of the pyrazole derivatives are presented in Table 3.

 E_{HOMO} is often associated with the electron donating ability of the molecule and a high value of the E_{HOMO} usually indicates a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy, empty molecular



Fig. 21 Optimized structures of the studied pyrazoles, DPC and DPCM



Scheme 4 Schematic representation of adsorption behavior of the studied pyrazoles on mild steel

	1		L	12		
Inhibitor	EI (%)	$V(A^{\circ^3})$	μ (D)	$E_{\rm HOMO}~({\rm eV})$	E_{LUMO} (eV)	$\Delta E (eV)$
DPC	73.09	211.85	5.40	-0.20866	-0.07304	0.13562
DPCM	97.14	282.18	5.11	-0.20625	-0.07079	0.13546

Table 3 Calculated quantum chemical parameters of the studied pyrazole derivatives

orbitals. On the other hand, E_{LUMO} , the energy of the lowest unoccupied molecular orbital, indicates the ability of molecule to accept electrons. The lower the value of E_{LUMO} , the more probable that the molecule accepts electrons [62, 63]. A low energy band gap value of <8.0 eV as estimated by the quantum mechanical method suggests stronger chemisorptions and good inhibition efficiency [64].

The value of dipole moment for pyrazoles is estimated to be of the order of 5.2 D, which indicates high compound polarity leading to greater inhibition [65, 66]. The HOMO and LUMO electronic density distributions of the two molecules are plotted

in Fig. 13. The occurrence of sufficiently high values of HOMO densities around the sulfur and nitrogen further indicates that these atoms behave as centers for chemisorptions [65].

Interaction and binding energy

Adsorption of DPC and DPCM heterocyclic molecules on iron surface (1 1 0) has been studied to find the lowest energy adsorption sites of these molecules on the steel under investigation. The geometry optimization for the two target inhibitors is carried out using an iterative process, where atomic coordinates are adjusted until and unless the total energy of individual structure reaches the minimum energy. Therefore, the selected molecules DPC and DPCM are placed on the iron surface (1 1 0) to discover the lowest energy adsorption sites along with their suitable configuration.

The equilibrium geometries for the complexes (Inh–Fe) in vacuum and aqueous solution were obtained using Becke's three-parameter exchange functional B3LYP with 6-31G (d) basis [61]. The effective contacts between the inhibitor molecules and the mild steel surface, as well as the best adsorption conformation for the both compounds, are presented in Figs. 22 and 23. As can be seen, the heteroatoms such as sulfur, nitrogen and oxygen play the main role of adsorption of inhibitors on the iron surface.

The interaction and binding energy (E_{Int} , E_{Bin}) between the inhibitor molecules and the Fe (1 1 0) surface was calculated for the minimum energy structure with the basis set superposition error (BSSE) and evaluated using the counterpoise method to eliminate basis functions overlap effects using Eqs. 10 and 11 [60, 67]:

$$E_{\rm Int} = E_{\rm Inh-Fe} - (E_{\rm Inh} + E_{\rm Fe}) \tag{10}$$

$$E_{\rm Bin} = -E_{\rm Int} \tag{11}$$

where $E_{\text{Inh-Fe}}$ is the total energy of the iron crystal together with the adsorbed inhibitor molecule, E_{Inh} and E_{Fe} are the total energy of the free inhibitor molecular and the iron crystal, respectively. The calculated interaction and binding energy values are listed in Table 4.

The calculated interaction energy values of the DPC-Fe and DPCM-Fe complexes in vacuum and HCl media are -27.37 and -34.13 kcal/mol and -40.51 and -43.99 kcal/mol, respectively. The hither negative values of interaction energy can be attributed to the strong adsorption between the pyrazole molecules and the iron surface [68]. DPCM has the highest interaction energy compared to DPC, which indicate that the DPCM molecule will give the best inhibition activity. Moreover, the higher value of binding energy for the DPCM (43.99 kcal/mol) inhibitor also suggests a more stable adsorption system for DPCM with higher inhibition efficiency [69]. The relative inhibition action of the studied molecules can be drawn from the parameters of interaction energy as well as binding energy. The stability of the inhibitor molecules and its inhibition efficiency



Fig. 22 The most stable configuration for adsorption of DPC inhibitor on the iron surface



Fig. 23 The most stable configuration for adsorption of DPCM inhibitor on the iron surface

are ranked as DPCM > DPC. These results confirmed that theoretical quantum chemical calculations are in good agreement with the experimental data [70]. In this way, we may infer that, of the two studied inhibitors, DPCM is more effective and can be strongly adsorbed on the iron surface through the pyrazole heterocyclic ring and the heteroatoms. The iron surface can be protected by the formation of an inhibitor layer which limits the attack from an aggressive solution.

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Systems	Interaction energy (kcal/mol)	Binding energy (kcal/mol)
Fe-DPC		
Vacuum	-27.37	27.37
HCl solution	-34.13	34.13
Fe-DPCM		
Vacuum	-40.51	40.51
HCl solution	-43.99	43.99

Table 4	Interaction	and binding	energy	values for	DPC and	DPCM	using 1	DFT	calculations
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Conclusions

Based on the above results, the following conclusions can be drawn:

- 1. Pyrazole derivatives were found to be inhibitors for mild steel corrosion in HCl solution. The inhibition efficiency increases with increasing concentration of DPC and DPCM at all temperatures studied. However, the inhibition efficiency of DPCM is increased with increasing temperature as a result of the performance of this inhibitor at higher temperatures in HCl medium.
- 2. The inhibition is probably due to the adsorption of the inhibitor on the metal surface and blocking its active sites by the phenomenon of chemi-physical adsorption.
- 3. Insertion of the methoxy group in the pyrazole structure increases inhibition efficiency. On the other hand, the methoxy group enhances the adsorption of DPCM on the surface of the steel under investigation.
- 4. Pyrazole derivatives are adsorptive inhibitors and their adsorption process obeys the Langmuir's adsorption isotherm, and is spontaneous.
- 5. All gravimetric measurements show that the DPCM is more effective than DPC in 1 M HCl.
- 6. The quantum chemical method shows that DPC and DPCM molecules can be directly adsorbed at the steel surface on the basis of donor-acceptor interactions between the π -electrons of the benzene ring, N and S atoms and the vacant *d*-orbitals of iron atoms.

References

- 1. G. Schmitt, Br. Corros. J. 19, 165 (1984)
- 2. H.H. Uhling, R.W. Revie, Corrosion and Corrosion Control (Wiley, New York, 1985)
- 3. V.S. Sastri, Corrosion Inhibitors, Principles and Applications (Wiley, New York, 1998)
- 4. A. Raman, P. Labine, M.A. Quraishi (eds.), *Reviews on Corrosion Inhibitor Science and Technology*, vol. 3 (Springer, Berlin, 2004)
- 5. M. Legrenee, B. Mernari, M. Bouanis, M. Traisnel, F. Bentiss, Corros. Sci. 44, 573 (2002)
- 6. N. Hackerman, Langmuir 3, 922 (1987)
- 7. M.A. Ameer, E. Khamis, G. Al Senani, Adsorpt. Sci. Technol. 18, 177-189 (2000)
- 8. M. Kissi, M. Bouklah, B. Hammouti, M. Benkaddour, Appl. Surf. Sci. 252, 4190-4198 (2006)
- 9. E.E. Oguzie, G.N. Onuoha, A.I. Onuchukwu, Mater. Chem. Phys. 89, 305-311 (2004)

- 10. E.E. Oguzie, Mater. Lett. 59, 1076-1079 (2005)
- 11. L. Tang, X. Li, G. Mu, G. Liu, L. Li, H. Liu, Y. Si, J. Mater. Sci. 41, 3063-3069 (2006)
- 12. E.E. Ebenso, Bull. Electrochem. 19, 209-216 (2003)
- 13. D.Q. Zhang, L.X. Gao, G.D. Zhou, J. Appl. Electrochem. 33, 361-366 (2003)
- 14. Y. Harek, L. Larabi, Kem. Ind. 53(2), 55-63 (2004)
- 15. M.A. Quraishi, F.A. Ansari, J. Appl. Electrochem. 36, 309-314 (2006)
- 16. M.A. Quraishi, M.Z.A. Rafiquee, N. Saxena, S. Khan, J. Corros. Sci. Eng. 10, 10-16 (2006)
- 17. S.S. Abd El Rehim, H.H. Hassan, M.A. Amin, Mater. Chem. Phys. 78, 337–348 (2002)
- F. Bentiss, M. Traisnel, N. Chaibi, B. Mernari, H. Vezin, M. Lagrenee, Corros. Sci. 44, 2271–2289 (2002)
- 19. M. Lebrini, M. Lagrenee, H. Vezin, L. Gengembre, F. Bentiss, Corros. Sci. 47, 485-505 (2005)
- H.B. Ouici, M. Belkhouda, O. Benali, R. Salghi, L. Bammou, A. Zarrouk, B. Hammouti, Res. Chem. Intermed. (2015). doi:10.1007/s11164-014-1556-2
- H.B. Ouici, O. Benali, Y. Harek, L. Larabi, B. Hammouti, A. Guendouzi, Res. Chem. Intermed. (2013). doi:10.1007/s11164-012-0797-1
- H.B. Ouici, O. Benali, Y. Harek, L. Larabi, B. Hammouti, A. Guendouzi, Res. Chem. Intermed. (2013). doi:10.1007/s11164-012-0821-5
- H.B. Ouici, O. Benali, A. Guendouzi, in AIP (American Institute of Physics) Conference Proceedings 1653, 020086 (2015). doi:10.1063/1.4914277
- 24. R. Solmaz, E. Altunbas, G. Kardas, Mater. Chem. Phys. 125, 796-801 (2011)
- 25. R. Solmaz, Corros. Sci. 52, 3321-3330 (2010)
- Moha Outirite, Michel Lagrenée, Mounim Lebrini, Michel Traisnel, Charafeddine Jama, Hervé Vezin, Fouad Bentiss, Electrochim. Acta 55, 1670–1681 (2010)
- 27. M.A. Quraishi, D. Jamal, Mater. Chem. Phys. 71, 202-205 (2001)
- H.B. Ouici, O. Benali, Y. Harek, S.S. Al-Deyab, L. Larabi, B. Hammouti, Int. J. Electrochem. Sci. 7, 2304–2319 (2012)
- 29. M. Abdallah, M.M. El-Naggar, Mater. Chem. Phys. 71, 291–298 (2001)
- 30. D.B. Hmamou, R. Salghi, A. Zarrouk, J. Environ. Chem. Eng. (2015). doi:10.1016/j.jece.2015.03.018
- 31. J. Cruz, R. Martínez, J. Genesca, E. García-Ochoa, Electroanal. Chem. 566, 111-118 (2004)
- 32. S.A. Abd El-Maksoud, A.S. Fouda, Mater. Chem. Phys. 93, 84–90 (2005)
- 33. E.A. Noor, A.H. Al-Moubaraki, Mater. Chem. Phys. 110, 145–154 (2008)
- 34. F. Bentiss, C. Jama, B. Mernari, H. El Attari, L. El Kadi, M. Lebrini, M. Traisnel, M. Lagrenee, Corros. Sci. 51, 1628–1635 (2009)
- 35. O. Benali, L. Larabi, M. Traisnel, L. Gengembra, Y. Harek, Appl. Surf. Sci. 253, 6130-6137 (2007)
- 36. F. Bentiss, M. Lebrini, M. Lagrenee, Corros. Sci. 47, 2915–2931 (2005)
- 37. W. Li, X. Lin, J. Wang, G. Li, Y. Wang, Synlett 13, 2003–2007 (2005)
- T.P. Robinson, R.B. Hubbard, T.J. Ehlers, J.L. Arbiser, D.J. Goldsmith, J.P. Bowen, Bioorg. Med. Chem. 13, 4007–4013 (2005)
- 39. D.I. Brahmbhatt, A.R. Kaneria, A.K. Patel, N.H. Patel, Indian J. Chem. 49B, 971–977 (2010)
- 40. O. El-Sabbagh, M.M. Baraka, S.M. Ibrahim, C. Pannecouque, Eur. J. Med. Chem. 44, 3746–3753 (2009)
- 41. X. Li, S. Deng, H. Fu, G. Muc, Corros. Sci. 51, 620-634 (2009)
- 42. O.K. Abiola, N.C. Oforka, S.S. Argaye, Mater. Lett. 58, 3461 (2004)
- 43. S.A. Umoren, I.B. Obot, E.E. Ebenso, N.O. Obi-Egbedi, Int. J. Electrochem. Sci. 3, 1029 (2008)
- 44. X.H. Li, G.N. Mu, Tween-40 as corrosion inhibitor for cold rolled steel in sulfuric acid: weight loss study, electrochemical characterization, and AFM. Appl. Surf. Sci. **252**, 1254–1265 (2005)
- 45. D.B. Hmamou, R. Salghi, A. Zarrouk, J. Environ. Chem. Eng. (2015). doi:10.1016/j.jece.2015.03.018
- 46. M.B. Valcarce, M. Vazquez, Mater. Chem. Phys. 115, 313–321 (2009)
- 47. W.A. Badawy, K.M. Ismail, A.M. Fathi, Electrochim. Acta 51, 4182-4189 (2006)
- 48. A. Azim, L.A. Shalaby, H. Abbas, Corros. Sci. 14, 21-24 (1974)
- 49. J. Flis, T. Zakroczymski, J. Electrochem. Soc. 143, 2458-2464 (1996)
- 50. M. Abdallah, Corros. Sci. 44, 717-728 (2002)
- H. Amar, A. Tounsi, A. Makayssi, A. Derja, J. Benzakour, A. Outzourhit, Corros. Sci. 49, 2936–2945 (2007)
- 52. S.K. Shukla, M.A. Quraishi, Corros. Sci. 51, 1990–1997 (2009)
- 53. S.K. Shukla, M.A. Quraishi, Corros. Sci. 51, 1007–1011 (2009)
- 54. E. Machnikova, K.H. Whitmire, N. Hackerman, Electrochim. Acta 53, 6024-6032 (2008)
- 55. I. Ahamad, M.A. Quraishi, Corros. Sci. 51, 2006–2013 (2009)
- 56. A.K. Singh, M.A. Quraishi, Corros. Sci. 51, 2752–2760 (2009)

- 57. R. Solmaz, G. Kardas, M. Culha, B. Yazici, M. Erbil, Electrochim. Acta 53, 5941-5952 (2008)
- 58. G. Avci, Colloid Surf. A Physicochem. Eng. Aspec. 317, 730-736 (2008)
- 59. A. Popova, M. Christov, S. Raicheva, E. Sokolova, Corros. Sci. 46, 1333–1350 (2004)
- 60. Gaussian 09, Revision A.1, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian, Inc., Wallingford CT, 2009
- 61. S.G. Zhang, W. Lei, M.Z. Xia, F.Y. Wang, J. Mol. Struct. (THEOCHEM) 732, 175-182 (2005)
- 62. M. Ozen, J. Dehri, M. Erbil, Appl. Surf. Sci. 236, 155 (2004)
- 63. I. Lukovits, K. Palfi, E. Kalma, Corrosion 53, 915 (1997)
- 64. G. Gao, C.H. Liang, Corros. Sci. 49, 33479 (2007)
- 65. R. Goel, W.A. Siddiqi, B. Ahmed, M.S. Khan, V.M. Chaubey, Desalination 263, 45-57 (2010)
- 66. F. Bentiss, M. Lagenee, M. Traibnel, C. Hornez, Corros. Sci. 41, 789 (1997)
- 67. H. Sun, J. Phys. Chem. B. 102, 7338-7364 (1998)
- 68. A.Y. Musa, A.A. Kadhum, H. Mohamad, M.S. Takriff, Corros. Sci. 52, 3331–3340 (2010)
- 69. K.F. Khaled, J. Appl. Electrochem. 41, 423-433 (2011)
- 70. X. Li, S. Fu, H. Deng, Corros. Sci. 53, 3241-3247 (2011)