

Pyrazole derivatives efficient organic inhibitors for corrosion in aggressive media: A comprehensive review

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Abstract

The high cost of corrosion estimated by billions of dollars per a year for industries. The research of new inhibitors to stop the increase of this phenomenon is more appreciate and tolerated during metallic materials use by human kind. Research of organic as well as mineral inhibitors increases more and more to stop or retard destruction of metals in aggressive media. Since 1995, our laboratory research had given an important thinking to solve this problem by using various techniques as weight loss, potentiodynamic and polarization resistance measurements. The focus was in using an organic inhibitor containing heteroatoms such as azoles derivatives, pyrazine; thiophene as well as extracts or oil of natural plants, *etc.* In this review, we report our contribution to this field by using pyrazole and bipyrazole derivatives as efficient and good inhibitors against corrosion in acidic media. Inhibitory effect depends on the constituent groups, metallic materials, corrosive medium. Pyrazole and bipyrazole compounds adsorb on the metallic surface according to physical and/or chemical process, and can also form organic-metal ion complexes. MarvinSketch.18 program was used in order to detect predominant form of inhibitors in electrolytic solution and then computed by Gaussian 09 based on the DFT method at B3LYP/6-31G(d,p) to correlate results obtained theoretically with those obtained experimentally.

Keywords: *pyrazole; organic inhibitors; inhibition; corrosion; acidic media; NaCl.*

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1. Introduction

Pyrazoles and bipyrazoles have attracted interest as ligands owing to the versatility of their coordination behavior towards a great variety of metals. Pyrazoles and bipyrazoles are regarded as one of the most flexible ligand systems in coordination chemistry due to their ease of synthesis and tunability of the substituents. These remarkable properties allowed to these materials a huge amount of applications. These lists are not exhaustive, for example, the pyrazole ligand was incorporated for preparing a novel advanced material for luminescent MOF compounds with specific engineering and design [1–6]. They presented also some biological activities such as modulators of CDK, GSK, aurora kinases and CCR1

antagonists [7–11]. They are useful in the treatment of diabetes and syndrome X and they are effective against renal disease [12–16]. They were also tested as herbicides in agrochemical components to 16 kinds of grasses [17–19]. The transport and extraction of Cd(II), Pb(II), and Hg(II) were also investigated using the pyrazole moieties [20–22]. They are the subject of many inventions related to use as contrast agents in imaging diagnosis [23–24]. These nitrogen compounds gain a lot of application in corrosion as a good organic inhibitor due to the presence of the labile electron doublet on the nitrogen. Accordingly, we now report a comprehensive review about pyrazole, bipyrazole and derivatives with the emphasize on their uses as good and an excellent organic inhibitor for corrosion in different media HCl, H₂SO₄, H₃PO₄, HNO₃ and NaCl.

2. Inhibition of corrosion by pyrazole derivatives in HCl media

Four industrially relevant pyrazole derivatives (**1–4**) differing in their nature of substituents were synthesized and their acid corrosion inhibition was studied for mild steel using experimental and computational approaches. Results revealed that the inhibition capability of these pyrazoles was substituent- and concentration-dependent. The inhibition efficiency followed the order: **4** (94.88%) > **3** (91.47%) > **2** (90.90%) > **1** (89.77%). By electrochemical studies these materials acted as mixed-type inhibitors and their adsorption obeyed the Langmuir isotherm. The DFT and MD simulations, and correlated with the experimental results [25] (Figure 1).

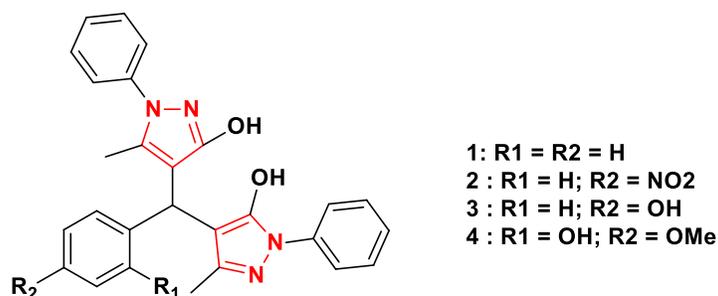
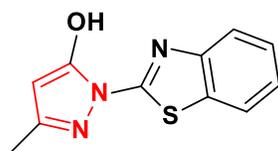


Figure 1. Structure of the pyrazoles **1–4** [25].

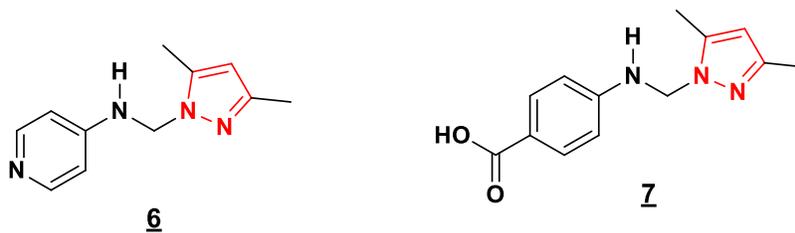
The 1-(2-benzothiazolyl)-3-methyl-pyrazol-5-one (**5**) (Figure 2) was synthesized and its ability to inhibit corrosion of ASTM A36 carbon steel in 1 mol·L⁻¹ HCl solution. The gravimetric method and quantum chemical parameters were used to evaluate the efficiency of the inhibitor and its adsorption capacity to the metal. Experimental results revealed that inhibition increases along with the concentration, reaching maximum inhibition of 93% at 600 mg·L⁻¹. In addition, it was observed that the adsorption of the compound **5** on the carbon steel surface obeys the Langmuir isotherm. Therefore, the theoretical and experimental results agree, showing that the inhibitor studied has a great anti-corrosion potential [26].



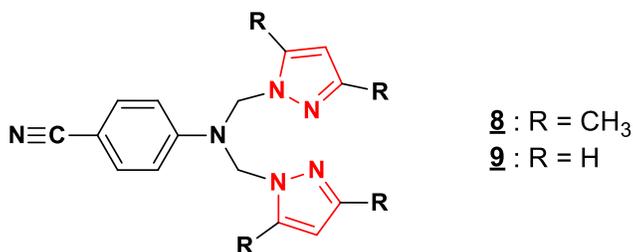
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Figure 2. Structure of compound **5** [26].

Pyrazole pyridine **6** and pyrazole benzoic acid **7** were synthesized and evaluated as corrosion inhibitors for mild steel in a 1 M HCl medium. The evaluation was performed by electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, and weight loss measurement. Both derivatives, **6** and **7**, showed good inhibition efficiency that is dependent on inhibitor concentration, acting as mixed-type inhibitors. The benzoic acid derivative **7** showed a higher efficiency than **6**, which could be attributed to the carboxyl group that is located at the para position to the amino group. Results also show that, they obey Langmuir adsorption isotherm. The relationship between the molecular structures and inhibition efficiencies of **6** and **7** were performed theoretically [27].

**Figure 3.** Structure of compounds **6**, **7** [27].

4-(bis((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)amino)benzotrile **8** and 4-(bis((1*H*-pyrazol-1-yl) methyl)amino)benzotrile **9** were prepared and have been studied for their inhibition efficiencies against corrosion of mild steel in 1 M HCl solution by weight loss and electrochemical measurements. The inhibition efficiency using weight loss measurement reached 92.4% for **8** and 92.3% for **9** at the highest concentration 10^{-3} M. They act as mixed type inhibitors according to the Langmuir adsorption isotherm. The impedance diagrams in the Nyquist presentation and DFT method have confirmed the experimental results [28].



8 : R = CH₃
9 : R = H

Figure 4. Structure of compounds **8**, **9** [28].

The 1-ethyl-1*H*-pyrazolo[3,4-*d*]pyrimidine-4(5*H*)-thione **10** and 1-methyl-4-methylsulfanyl-1*H*-pyrazolo[3,4-*d*]pyrimidine **11** have been evaluated as corrosion inhibitor for mild steel in 1 M HCl solution by means of potentiodynamic polarization and electrochemical impedance spectroscopic measurements. The obtained results revealed that this compound is a good mixed type inhibitor with cathodic predominance effectiveness. The effect of temperature on the corrosion behavior with the addition of optimal concentration of 10^{-3} M was studied in temperature range of 303–343 K. The value of inhibition efficiency decreases slightly with the increasing of temperature. The adsorption of the inhibitor on the mild steel (MS) surface follows the Langmuir adsorption isotherm, indicating monolayer adsorption. The activation parameters indicate the inhibitor is physically adsorbed. Quantum chemical calculations were used to correlate the inhibition ability of **11** with its electronic structural parameters [29, 30].

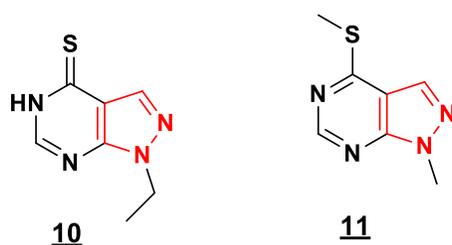


Figure 5. Structure of compounds **10** and **11** [29, 30].

The inhibition performance and mechanism of N1,N1,N3,N3-tetrakis((3,5-dimethyl-1*H* pyrazol-1-yl)methyl)propane-1,3-diamine **12** and N1,N1,N2,N2-tetrakis((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)benzene-1,2-diamine **13** for the corrosion of mild steel in 1 M HCl were investigated using weight loss method and electrochemical measurements. The results show that both tetrakis pyrazole derivatives act as good inhibitors, and inhibition efficiency follows the order: **13** > **12**. Two tetrakis pyrazole derivatives are mixed type inhibitors exhibiting predominantly cathodic behavior. The Nyquist plots showed that, after increasing inhibitor's concentrations, charge-transfer resistance increased and double-layer capacitance decreased, involving increased inhibition efficiency. The adsorption of both inhibitors on a steel surface obeyed Langmuir model, and theoretically studies in good correlation with experimental results [31].

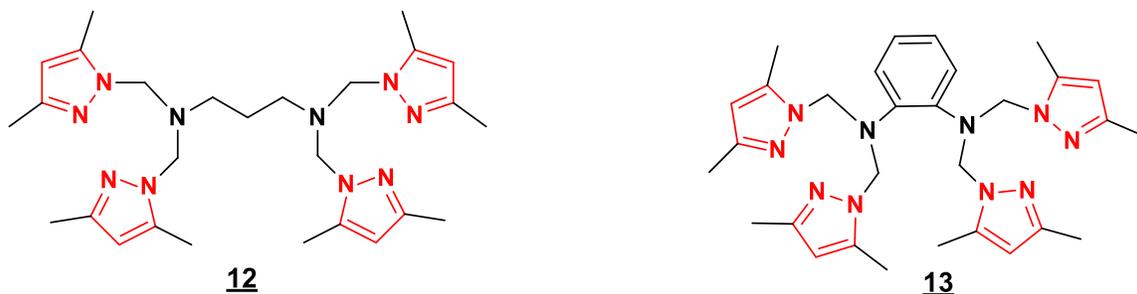


Figure 6. Structure of compounds **12** and **13** [31].

A new corrosion inhibitor namely 2-[Bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-amino]-3-hydroxy-butyric acid **14** has been synthesized and investigated its inhibitive performance towards the corrosion of carbon steel in 1 M hydrochloric acid using usual techniques. The efficiency of the inhibitor increases with increase in the inhibitor concentration. Results obtained reveal that the used Bipyrazole derivative performs as corrosion inhibitor for carbon steel in 1 M HCl. The adsorption of this compound on carbon steel surface is found to obey Langmuir adsorption isotherm [32].

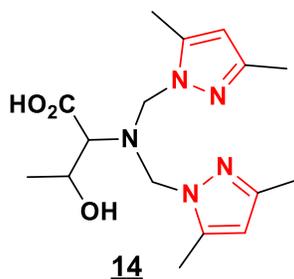


Figure 7. Structure of compound **14** [32].

The $\{N,N'$ -bis-[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]- N,N' -dimethylethane-1,2-diamine **15** and N,N' -bis[(3-ethylcarboxylate-5-methyl-1*H*-pyrazol-1-yl)methyl]- N,N' -dimethyl ethane-1,2-diamine **16** have been studied as organic inhibitors for corrosion for mild steel in 1 M HCl. All the techniques employed are in good agreement between them. The protection efficiency rises with increasing inhibitors concentrations and increasing temperature too [33]

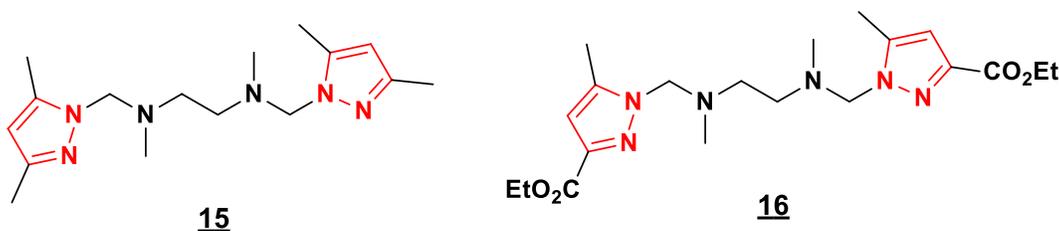


Figure 8. Structure of compounds **15**, **16** [33].

The quantum chemical calculations based on the DFT method on two bipyrazoles **17**–**18** used as corrosion inhibitors for the plain carbon (“mild”) steel in acid media. This study shows the relationship between inhibition efficiency and the molecular structure of inhibitors are in good agreement [34].

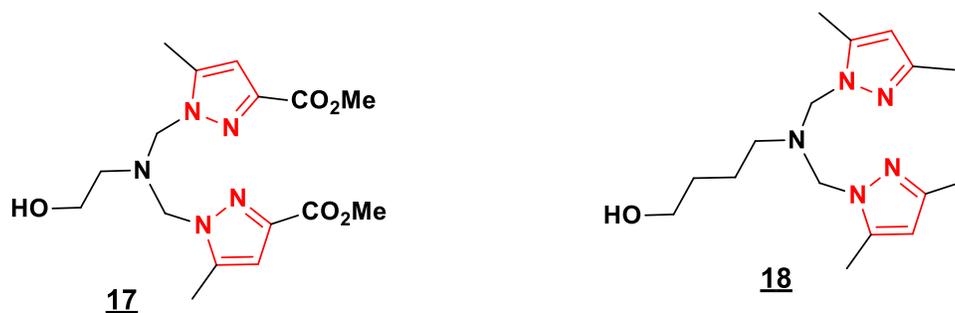


Figure 9. Structure of compounds **17**, **18** [34].

The effect of synthesized 1,1'-propane-1,3-diylbis[3-(chloromethyl)-5-methyl-1*H*-pyrazole] **19**, dimethyl 1,1'-butane-1,4-diylbis(5-methyl-1*H*-pyrazole-3-carboxylate) **20** and 1,1'-butane-1,4-diylbis[3-(chloromethyl)-5-methyl-1*H*-pyrazole] **21** on corrosion of C38 steel in hydrochloric acid solution has been investigated in the temperature range from 298 K to 328 K by weight loss, potentiodynamic polarization method and modelled with an equivalent electric circuit. All the compounds exhibited more than 90% anticorrosion activity, the highest is 96% by **21**, and it has been shown that the inhibition efficiencies increased with the concentration of the inhibitors, remaining almost constant in a wide temperature range. Potentiodynamic polarization studies suggested that it is a predominance cathodic type. Nyquist plots showed depressed semicircles with their center below the real axis. The adsorption on the C38 steel surface followed the Langmuir adsorption isotherm. The thermodynamic parameters for dissolution were investigated at different concentrations and temperature. The theoretical study by modelling the molecules of these inhibitors has been performed by considering the Density Functional Theory (DFT) using the Gaussian 03W suite of programs that can calculate the different quantum parameters such as E_{HOMO} , E_{LUMO} , $D E_{\text{HOMO}}$, E_{LUMO} , and μ dipolar moment, allowing us to confirm the results found by the gravimetric and electrochemical methods [35].

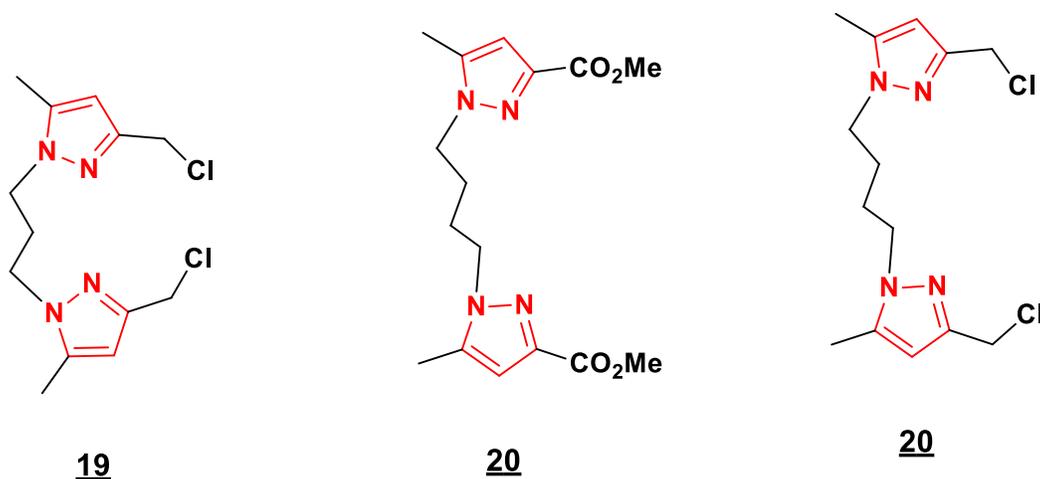


Figure 10. Structure of compounds **19**, **20** [35].

The corrosion inhibition of mild steel in 1 M HCl solution by *N,N'*-bis[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]piperazine **21** and *N,N'*-bis[(3-ethylcarboxylate-5-methyl-1*H*-pyrazol-1-yl)methyl]piperazine **22** was studied using usual techniques. These measurements show that the inhibition efficiency obtained by these compounds increased by increasing their concentrations. to attain 91% for **21** and 92% for **22** since 10^{-3} M [36].

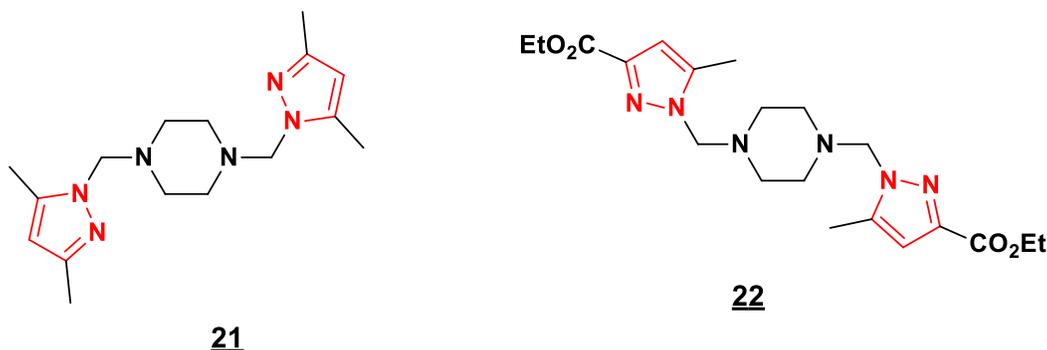


Figure 11. Structure of compounds **21**, **22** [36].

Three bipyrazole derivatives, 1,1',5,5'-tetramethyl-1*H*,1'*H*-3,3'-bipyrazole **23**, Ethyl-5,5'-dimethyl-1'*H*-1,3'-bipyrazole-4-carboxylate **24**, and 3-(bromomethyl)-5,5'-dimethyl-1'*H*-1,3'-bipyrazole **25**, have been synthesized and used as additives to protect C38 steel from corrosion in aerated 1 M HCl solution, using the various corrosion monitoring techniques such as weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy. All the techniques used for the studies show an increase in inhibition efficiency and decrease in the corrosion rate by increasing the inhibitor concentration [37, 38].

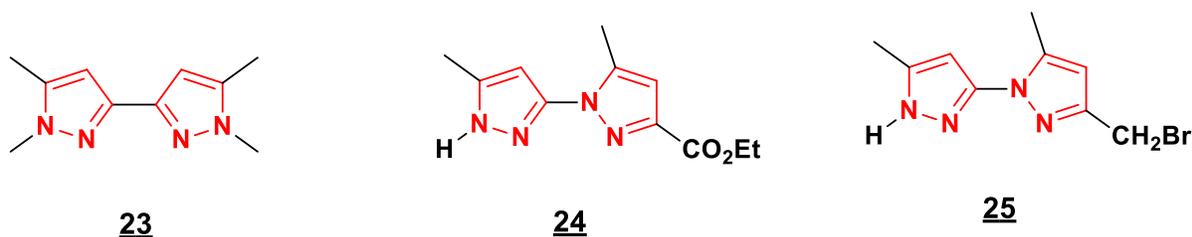


Figure 12. Structure of compounds **23–25** [37, 38].

The corrosion and inhibitors adsorption processes in mild steel of two tripodal pyrazolic compounds 3-[bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-amino]-propan-1-ol **26** and 1-[bis-(3-carbomethoxy-5-methyl-pyrazol-1-ylmethyl)-amino]-propan-2-ol **27** in hydrochloric acid solution were studied at different temperatures (308–323 K) by means weight loss (WL) measurements. It has been found that the studied compounds exhibit a very good performance as inhibitors for mild steel corrosion in 1 M HCl. These results show that the inhibition efficiency increases with decreasing temperature and increasing concentration of inhibitors. It has been determined that the adsorption for the studied inhibitors on mild steel

complies with the Langmuir adsorption. The kinetic and thermodynamic parameters for mild steel corrosion and inhibitor adsorption were determined and discussed, respectively. On the bases of thermodynamic adsorption parameters, comprehensive adsorption (physisorption and chemisorption) for the studied inhibitors on mild steel surface has been suggested [39].

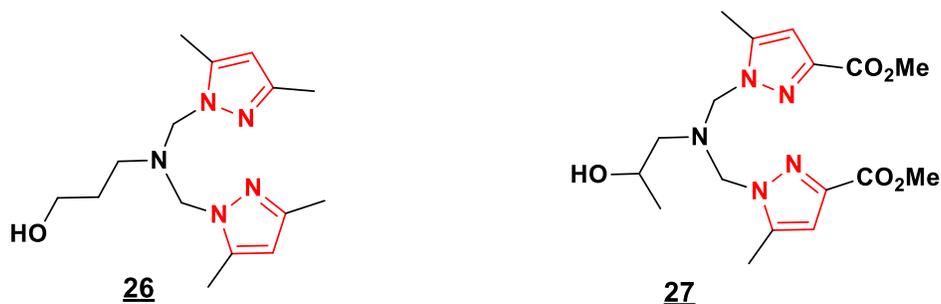


Figure 13. Structure of compounds **26**, **27** [39].

Corrosion inhibition of copper through six bipyrazolic compounds **28–33** has been elucidated by means of density functional theory (DFT)-derived reactivity indexes. The DFT calculated parameters and experimental corrosion inhibition efficiency ($IE\%$) indicate that their inhibition effect is closely related to the frontier orbital energies, polarizability, electronic chemical potential and global nucleophilicity. The quantum chemistry calculations were performed at the B3LYP/6-31G (d) level. The theoretical results, predicted using DFT-based reactivity indexes, are in good agreement with experimental outcomes [40, 41].

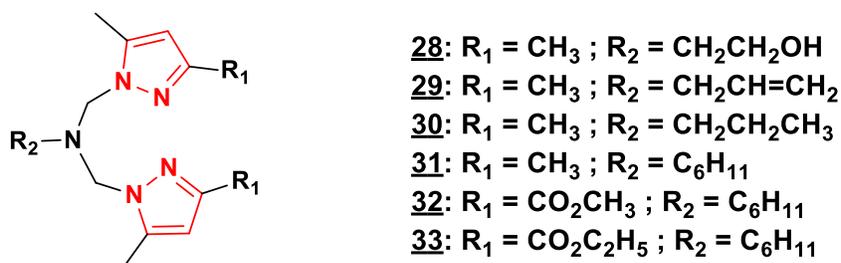


Figure 14. Structure of compounds **28–33** [40, 41].

The effect of some prepd. compounds, 3,5-dimethyl-1*H*-pyrazole **34**, 3(5)-amino-5(3)-methylpyrazole **35**, and 1',3,5,5'-tetramethyl-1'*H*-1,3'-bipyrazole **36**, on the corrosion behavior of steel in 1 M HCl solution as corrosive medium was studied at 308 K using weight loss measurement, potentiodynamic polarization, linear polarization, and impedance spectroscopy (EIS). Generally, inhibition efficiency of the studied compounds depends on the concentration and nature of the inhibitor. The compound **36** was a better inhibitor than **34** and **35**, and its inhibition efficiency increased with increasing concentration of inhibitor [42].

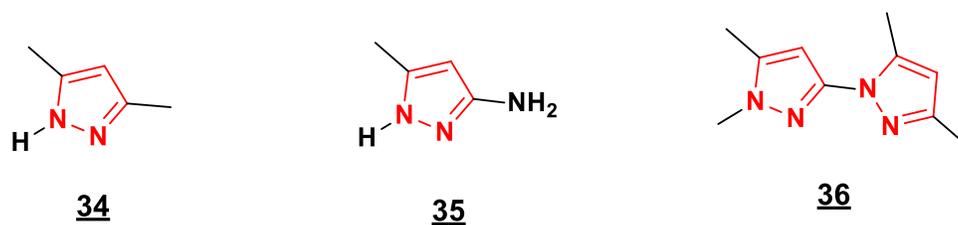


Figure 15. Structure of compounds **34–36** [42].

The inhibitor effect of two isomers namely 2-(1',5,5'-trimethyl-1H,1'H-3,3'-bipyrazol-1-yl)ethanol **37** and 2-(1',5,5'-trimethyl-1H,2'H-3,3'-bipyrazol-2-yl)ethanol **38** on the corrosion of mild steel in 1 M hydrochloric acid was investigated at 308 K using weight loss measurements and electrochemical techniques. Inhibition efficiency is dependent upon the pyrazole structure, with **37** serving as a better inhibitor than **38** and its inhibition efficiency increases with the increase of concentration of inhibitor to attain 93% in the presence of 10^{-3} M [43].

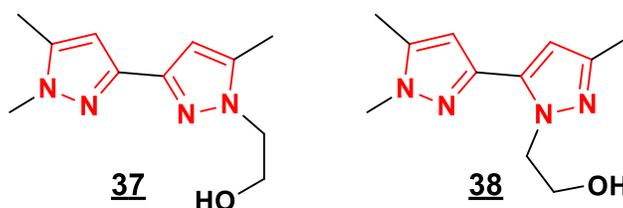


Figure 16. Structure of compounds **37, 38** [43].

In this study, some possible relationship between the experimental inhibition corrosion in acidic media and the theoretical energy calculations DFT, for six compounds **39–44** has been presented. These sets of compounds have been tested for their corrosion inhibition properties of steel in low concentration of hydrochloric acid medium [44].

A theoretical study of five bipyrazolic-type organic compounds, 4-{bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-amino}phenol **45**, *N1,N1*-{bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]}-*N4,N4*-dimethyl-1,4-benzenediamine **46**, *N,N*-bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]aniline **47**, 4-[bis(3,5-di-Me-pyrazol-1-yl-methyl)-amino]butan-1-ol **18**, ethyl-4-[bis(3,5-dimethyl-1H-pyrazol-1-yl-methyl)aminobenzoate] **48**, and *N*-benzyl-*N,N*-bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]amine **49** on the corrosion of steel in 1 M HCl was studied at 308 K. Weight loss measurements, potentiodynamic polarization, and have been performed using (DFT) in order to elucidate the different inhibition efficiencies and reactive sites of these compounds [45–47].

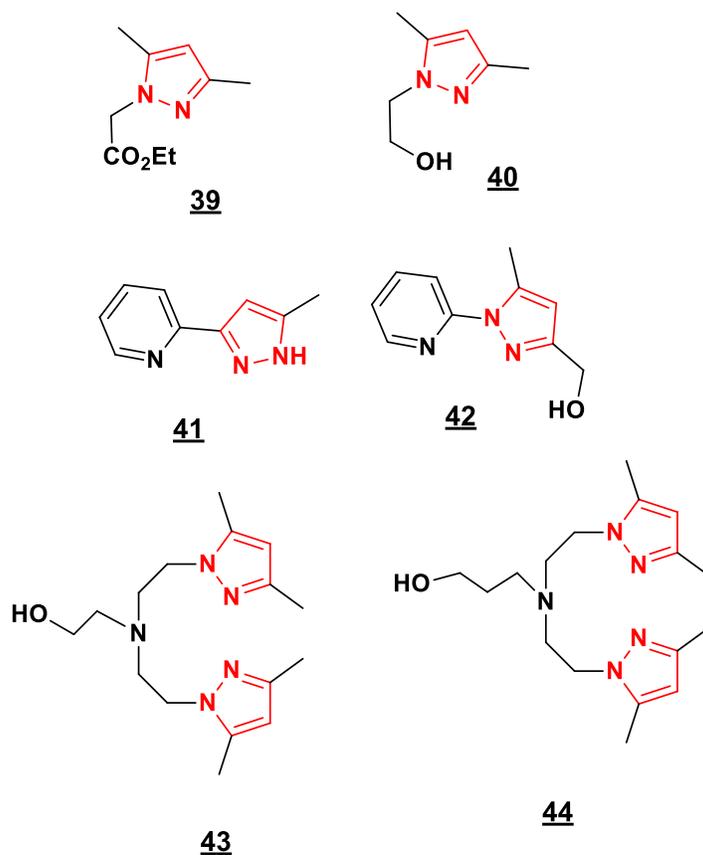


Figure 17. Structure of compounds 39–43 [44].

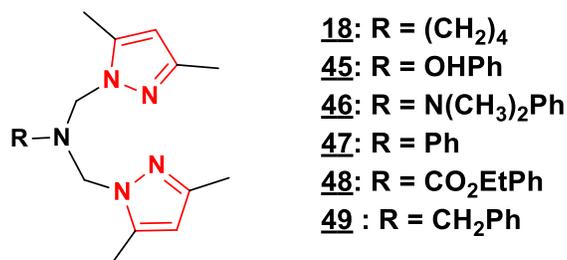


Figure 18. Structure of compounds 18, 45–49 [45–47].

Potentiodynamic polarization, electrochemical impedance spectroscopy and weight loss studies were carried out on the inhibition of carbon steel in 1 M HCl solution by 5,5-dipropyl-1*H*,1*H*-[3,3]bipyrazolyl **50**, 5,5-diphenyl-1*H*,1*H*-[3,3]bipyrazolyl **51** and 5,5-bis-(4-chloro-phenyl)-1*H*,1*H*-[3,3]bipyrazolyl **52**. All measurements show that inhibition efficiency increases with increase in inhibitor concentration and the variation in inhibitive efficiency mainly depends on the type and nature of the substituents present in the inhibitor molecule to attain 98% for chloro derivative **52** at 10⁻³ M. This reveals that inhibitive actions of bipyrazolic compounds were mainly due to adsorption on steel surface and theoretical investigations were well correlated with the experimental ones [48].

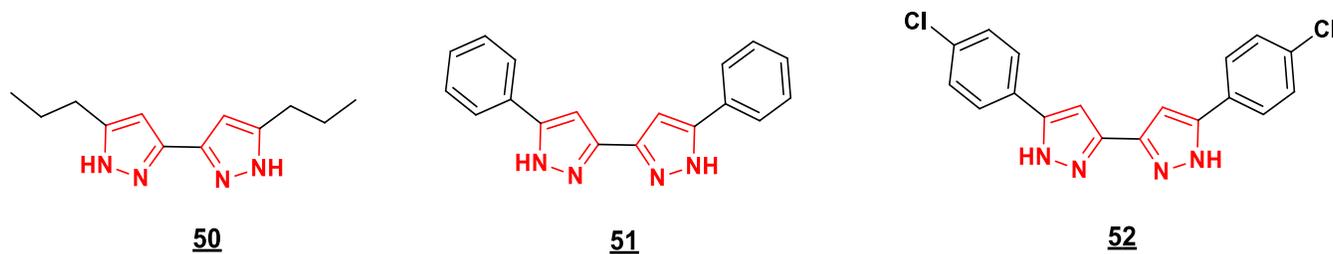


Figure 19. Structure of compounds **50–52** [48].

The influence of 3,5-dimethyl-1*H*-pyrazole **53**, and 2-(3-methyl-1*H*-pyrazol-5-yl)pyridine **54** on the corrosion inhibition of carbon steel in 1 M HCl solution was studied by using weight-loss, potentiodynamic and EIS measurements. The compound **34** was the best inhibitor, and its inhibition efficiency increases with increasing inhibitor concentration to attain 89% at 10^{-3} M. Potentiodynamic polarization studies clearly reveal that it acts essentially as a cathodic inhibitor. The efficiency values obtained by the various methods used were in agreement [49].

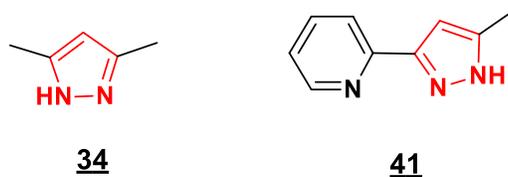


Figure 20. Structure of compounds **41, 34** [49].

The study the effect of inhibition of new bipyrazole derivatives on the corrosion of steel in HCl media at various temperature. The design of novel corrosion inhibitors, bipyrazoles were tested as corrosion inhibitors for steel in 1 M HCl, ethyl-5,5'-dimethyl-1'*H*-1,3'-bipyrazole-3-carboxylate **24** and 3,5,5'-trimethyl-1'*H*-1,3'-bipyrazole **54**, 1,5,5'-trimethyl-1*H*,2'*H*-3,3'-bipyrazole **55**, ethyl 1',5,5'-trimethyl-1'*H*-1,3'-bipyrazole-3-carboxylate **56** and 1',5,5'-trimethyl-1'*H*-1,3'-bipyrazol-3-yl)methanol **57** on the corrosion behavior of steel in 1 M HCl solution was studied at 308 K by weight loss measurements, potentiodynamic polarization and impedance spectroscopy (EIS) methods. The inhibition efficiencies obtained from cathodic Tafel plots, gravimetric and EIS methods are in good agreement. The compound **54** is the best inhibitor and its efficiency reaches 84% at 10^{-3} M and acts as cathodic-type inhibitors [50, 51].

The inhibiting action of six bipyrazolic isomers, namely, 4-{bis[(1,5-dimethyl-1*H*-pyrazolyl-3-yl)methyl]amino}phenol **58**, 4-{bis[(3,5-dimethyl-1*H*-pyrazolyl-1-yl)methyl]amino}phenol **45**, *N,N*-bis[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]-*N*-(4-methylphenyl)amine **61** and methyl 1-[[[(methylphenyl){3-(methoxycarbonyl)-5-methyl-1*H*-pyrazol-1-yl]methyl]amino)methyl]-5-methyl-1*H*-pyrazole-3-carboxylate **60** for the corrosion of steel in 1 M HCl solution has been investigated at 308 K by using weight loss measurements, polarization and impedance spectroscopy methods. The inhibition efficiencies evaluated from the methods used are in agreement. The polarization curves reveal that these

bipyrazolic compounds **45**, **58**, **60–63** act as mixed-type inhibitors and are efficient inhibitors. Their inhibition efficiencies reached *ca.* 95% for both isomers at $5 \cdot 10^{-4}$ M concentration (308–353 K) [52–54].

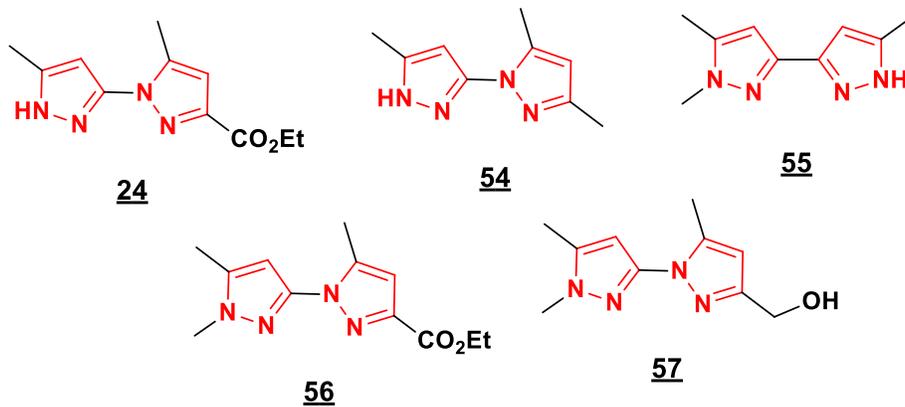


Figure 21. Structure of compounds **24**, **54–57** [50, 51].

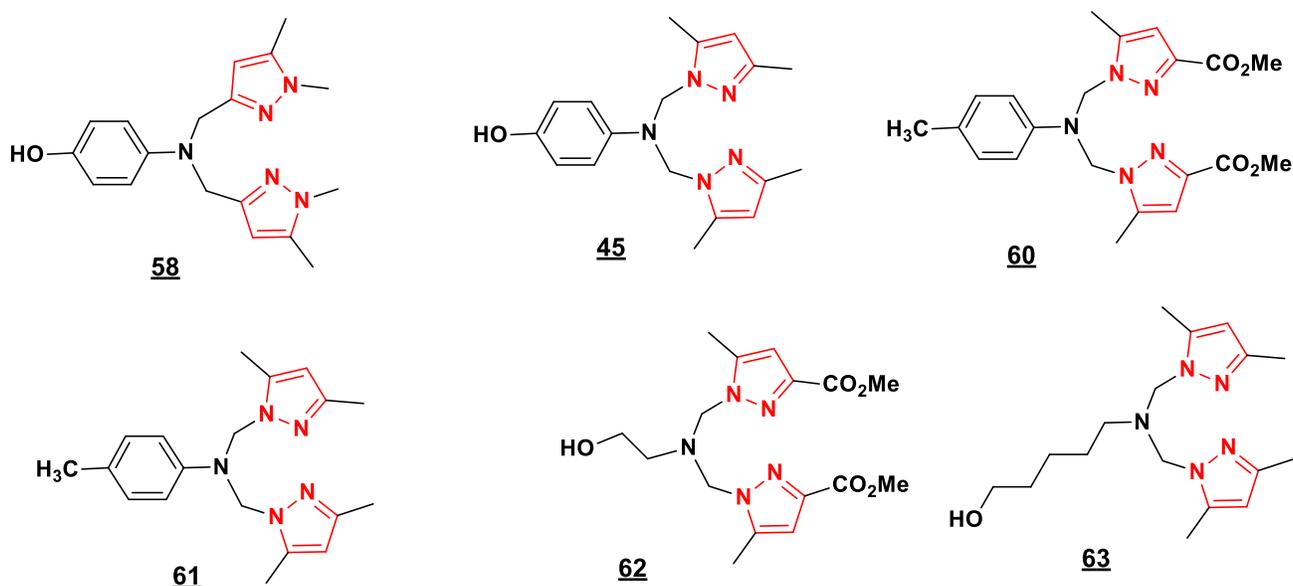


Figure 22. Structure of compounds **45**, **58**, **60–63** [52, 54].

The inhibition of the corrosion of steel in 1 M HCl by two pyridine-pyrazole type organic compounds (5-methyl-1-pyridin-2-yl-1*H*-pyrazol-3-yl)methanol **64** and ethyl 5-methyl-1-pyridin-2-yl-1*H*-pyrazol-3-carboxylate **65** has been studied at 308 K by weight loss, electrochemical polarization, polarization resistance and electrochemical impedance spectroscopy (EIS) measurements. The inhibition efficiencies obtained from cathodic Tafel plots gravimetric and EIS methods were in good agreement. The results obtained reveal that these compounds are efficient inhibitors. The inhibition efficiency increases with the increase of inhibitor concentration and reached 94% for **64** at 10^{-3} M. Potentiodynamic polarization studies clearly reveal that the presence of inhibitors **63** and **64** does not change

the mechanism of hydrogen evolution and that they act essentially as cathodic inhibitors. The inhibitors were adsorbed on the steel surface according to the Frumkin adsorption isotherm model [55].

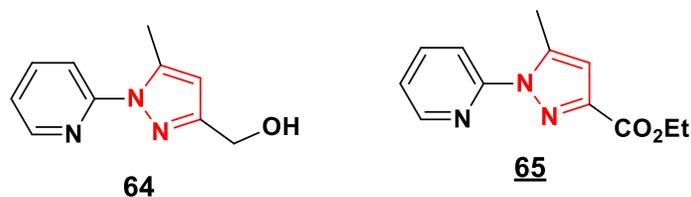


Figure 23. Structure of compounds **64–65** [55].

The inhibition of corrosion of steel in 1 M HCl solution by pyrazole derivatives **63** and **66** was studied by weight loss and polarization techniques at 308 K. The results obtained reveal that tripyrazole exhibits a good protection. Inhibition is found to increase with increase in inhibitor concentration. The inhibition behavior of the compound was explained on the basis of molecular size and charge distribution of adsorption active centers. The adsorption phenomenon obeys the Langmuir adsorption isotherm model [56].

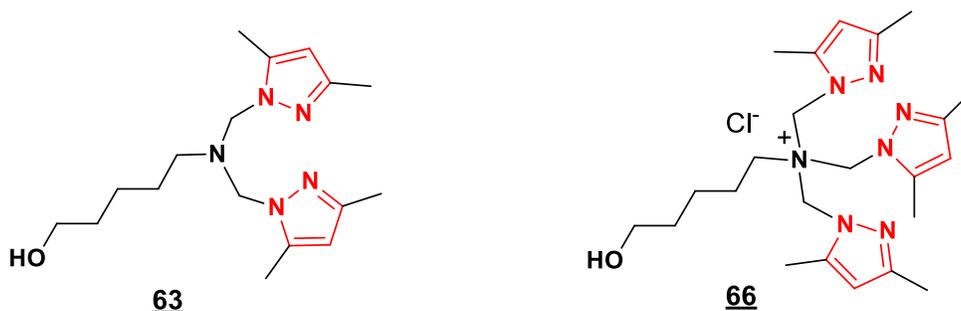


Figure 24. Structure of compounds **63, 66** [56].

Bipyrazolic compounds **19, 67–69** were tested as corrosion inhibitors for lead in 0.3 M hydrochloride acid using potentiodynamic measurement and gravimetric methods. Results obtained showed that bis(3-carbomethoxy-5-methyl-1-pyrazolyl)methane **67** was the best inhibitor and its inhibition efficiency reaches a value of 88% at 10^{-3} M. Polarization measurements indicated that the *c.d.* decreases with increasing inhibitor concentration all these ligands were adsorbed on the lead surface according to a Langmuir isotherm model. The effect of temperature indicated that inhibition efficiency of these compounds decreases with increasing temperature at 298–343 K [57–65].

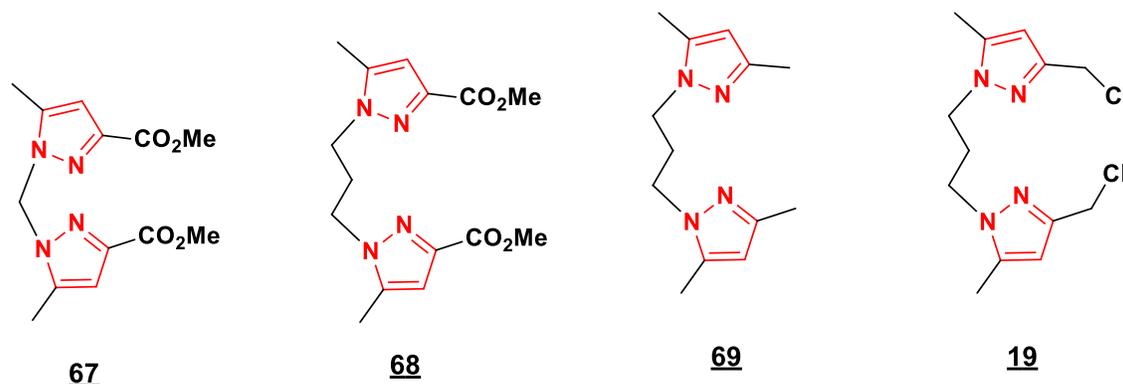


Figure 25. Structure of compounds 19, 67–69 [57–65].

3. Inhibition of corrosion by pyrazole moieties in H₂SO₄ media

The corrosion inhibition of mild steel in 0.5 M H₂SO₄ using ethyl 1-(((4-acetylphenyl)-((3-(ethoxycarbonyl)-1*H*-pyrazol-1-yl)methyl)amino)methyl)-5-methyl-1*H*-pyrazole-3-carboxylate **70** at 298 K have been investigated. The study was performed using weight loss method, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS). The experimental results suggest that the inhibition efficiency of this compound increases with the increase in inhibitor concentration. Adsorption of this compound on mild steel surface obeys Langmuir's isotherm. Polarization measurements proved that this inhibitor behave as mixed type. EIS data showed that the charge transfer resistance of mild steel increases in acid solution containing inhibitor. Correlation between quantum chemical calculations and inhibition efficiency of the investigated compound is discussed using the Density Functional Theory method (DFT) [66].

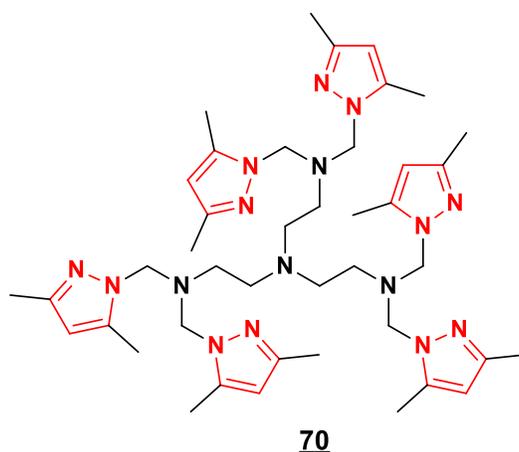


Figure 26. Structure of compound 70 [66].

The corrosion inhibition of mild steel in 0.5 M H₂SO₄ in the presence of *N*1,*N*1-bis(2-bis((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)amino)ethyl)-*N*2,*N*2-bis((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)ethane-1,2-diamine **71** has been studied by electrochemical techniques (DC polarization and AC impedance) and weight loss measurement. Result obtained reveal

that this pyrazole derivative is good inhibitor for mild steel in 0.5 M H₂SO₄. Tafel polarization studies clearly reveal the type of inhibitor. This pyrazole derivative acts on cathodic and anodic reactions and reduces corrosion current density. Changes in impedance parameters (R_{ct} and C_{dl}) are indicative of adsorption of the pyrazole derivative on the metal surface leading to formation of protective film which grows with increasing concentration and inhibition efficiency values increase. The effect of temperature on the corrosion behavior of mild steel with the addition of the pyrazole derivative was studied in the temperature range from 303 to 333 K. Thermodynamic parameters for adsorption and activation processes were determined. Adsorption of this inhibitor follows the Langmuir adsorption isotherm [67].

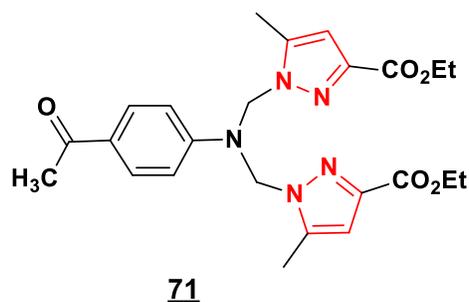


Figure 27. Structure of compound **71** [67].

The 2-[bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-amino]-4-[bis-(3,5-dimethyl-pyrazol-1-ylmethyl)carbamoyl]-butyric acid **72** has been evaluated as a corrosion inhibitor for carbon steel using weight loss and electrochemical polarization (EIS). The study was also complemented by SEM (SEM) and quantum chemical calculations. The inhibition efficiency ($\eta\%$) increased with increasing **72** concentration, showing a maximum IE of 93.5% at 298 K at 10^{-3} M and decreased with increasing temperature. The electrochemical studies showed that **72** inhibitor retards both cathodic and anodic processes through the inhibitor adsorption on the surface [68].

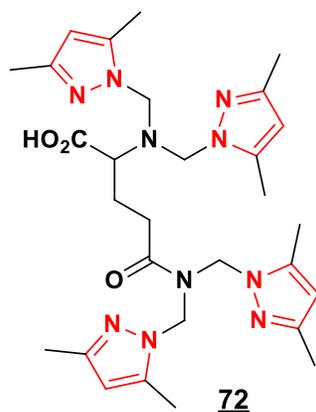
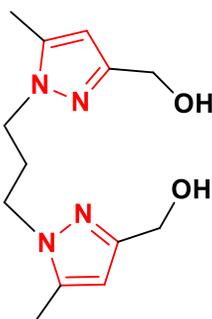


Figure 28. Structure of compound **72** [68].

The effect of addition of 1,3-bis(3-hydroxymethyl-5-methyl-1-pyrazole) propane **72** on steel corrosion in 0.5 M sulfuric acid is studied by weight loss, electrochemical polarization and electrochemical impedance spectroscopy (EIS) measurements at various temps. The results obtained showed that **72** acts as a good corrosion inhibitor. The inhibition efficiency increases with the bipyrazole compd. to attain 88%. It acts as a mixed-type inhibitor. Trends in the increase of charge-transfer resistance and decrease of capacitance values also show the adsorption of the molecule on the metal surface. The bipyrazole adsorbs on the steel surface according to the Langmuir isotherm adsorption model. Effect of temperature indicates that inhibition efficiency decreases with temp. between 25 and 85°C [69].



73

Figure 29. Structure of compound **73** [69].

4. Inhibition of corrosion by pyrazole moieties in NaCl media

The corrosion behavior of copper in aerated 3% NaCl solution was investigated by rotating electrode at various rates. The rendement of O₂ obeys the Levich equation. The inhibition of the copper corrosion in aerated 3% NaCl solution was studied by using potentiodynamic polarization and linear polarization resistance (LRP) in the presence of different concentrations of a bipyrazolic compound named N,N-bis(3-carbomethoxy-5-methylpyrazol-1-ylmethyl)cyclohexylamine **33** (Figure 15). The presence of this compound in the solution decreases the corrosion *c.d.* and increases the linear resistance polarization [70]. The inhibition of the copper corrosion in aerated 3% NaCl solution was studied by using electrochemical polarization, weight loss and impedance measurements in the presence of different concentration of synthesized bipyrazolic compounds (Figure 15). The inhibition efficiencies obtained from cathodic Tafel plots, polarization resistance and weight loss are in agreement with electrochemical impedance spectroscopy measurements. All these additives were excellent inhibitors for copper corrosion. The difference in inhibition efficiencies of these inhibitors was not large, but the optimum concentration for maximum efficiency was slightly dependent on the substitution of each molecule. The studied molecules act as mixed-type inhibitors. Detailed study of inhibition shows that the maximum inhibition efficiency was approximately 99% with 5.10⁻⁴ M of inhibitor. The latter adsorbs

on the copper surface according to the Frumkin isotherm model. The inhibition efficiency of inhibitors decreases with increasing temperatures in the range 25–60°C [71].

4. Inhibition of corrosion by pyrazole moieties in H₃PO₄ media

The effect of a ruthenium-ligand complex **74** on the corrosion of steel in 2 M H₃PO₄ has been investigated at various temperatures using electrochemical techniques (impedance spectroscopy (EIS), polarization curves) and weight loss measurements. Inhibition efficiency (*E*%) increases with **74** concentration to attain 90% at 5×10⁻⁴ M. EIS measurements show that the dissolution process of steel occurs under activation control. Polarization curves indicate that **74** acts as a cathodic inhibitor. *E*% values obtained from various methods used are in good agreement. The temperature effect on the corrosion behavior of steel in 2 M H₃PO₄ without and with the inhibitor at various concentrations was studied in the temperature range from 298 to 338 K. Thermodynamic parameters such as adsorption heat (ΔH_{ads}), adsorption entropy (ΔS_{ads}) and adsorption free energy (ΔG_{ads}) have been calculated. Kinetic parameters for the corrosion reaction at different concentrations of **74** were determined. Adsorption of **74** on the mild steel surface in 2 M H₃PO₄ follows the Langmuir isotherm model [72].

Pyrazole compounds received recently more attention by researchers in corrosion protection as well as biological activities [73–80]. Pyrazole compounds form on the metallic surface according to physical and/or chemical layer, and the formation organic-metal ion complexes at the surface can explain the decrease of current densities at anodic branch. The DFT method at B3LYP/6-31G (d,p) is an important tool to correlate results obtained theoretically with those obtained experimentally.

The nature of mineral acid affects the inhibitory action of organic inhibitor, in fact, the most studied pyrazole derivatives acted as mixed type inhibitors in HCl media, can lose activity on anodic reaction, this behavior may be explained by the nature of counter ion of H⁺ as Cl⁻, HSO₄⁻, H₂PO₄⁻, HPO₄²⁻ ... Cl⁻ is known as non-alkaline ion, the others have alkaline effect at the metal surface.

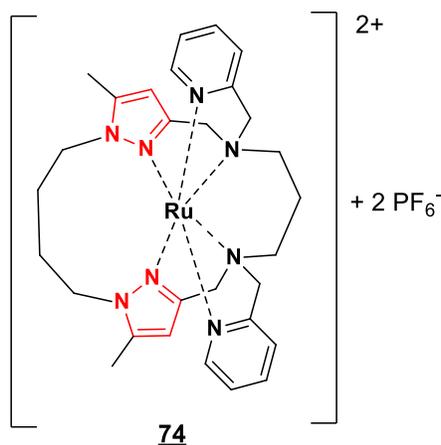


Figure 30. Structure of compound **7** [72].

Conclusion

The inhibitory effect of pyrazole derivatives on the corrosion of different metals in HCl, H₂SO₄, H₃PO₄ and NaCl medium was studied by weight loss, electrochemical polarization and impedance studies. The maximum inhibition efficiency depends on the increase of the inhibitor concentration and the temperature. The inhibition effect is caused by geometrically blocking the surface of metal by adsorbed inhibitive molecules, which follow Langmuir isotherm model. The quantum calculations DFT and theoretically studies were in good correlation with experimental ones.

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