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Synthesis, antioxidant and anticorrosion activities of two nitrogen organic compounds

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Abstract

The purpose of this research was to study antioxidant as well as anticorrosive activities of two synthesized pyrazoline derivatives compounds. The antioxidant capacity was evaluated by four complementary tests including " 2,2-diphenyl-1-picrylhydrazyl (DPPH) , cupric-reducing antioxidant capacity (CUPRAC), 2,2'-azinobis (3-ethylbenzothiazoline-6-sulfonate) (ABTS+) radical cation and O^{2-} in dimethyl sulfoxide (DMSO) alkaline assays". The inhibiting effect of the two compounds on carbon steel in 1M HCl solution was investigated by weight loss measurement. The obtained results revealed that the compound P1 has the best antioxidant activity compared to P2. It was found also that the inhibition efficiency increases with an increase in concentration of inhibitors and follow the order P1 > P2. The adsorption of the inhibitors on the carbon steel surface obeys Langmuir adsorption isotherm and occurred via both physical and chemical adsorption.

Keywords: Pyrazoline derivatives, Antioxidant, DPPH, Corrosion inhibitors, Carbon steel

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1. Introduction

Over the years considerable efforts have been devoted to design and synthesize functional nitrogenous compounds possessing extensive biological, pharmacological activities and various applications in industries [1]. Pyrazolines and their analogues represent an important class of nitrogenous compounds obtained by the efficient reaction of α, β-unsaturated carbonyl compounds with diazoalkanes or with hydrazine hydrate [2]. They have large potential applications in various areas such as: medicine, agriculture and analytical chemistry. Pyrazolines are used as optical brighteners and whiteners. They display various biological activities such as antimicrobial [3], antifungal [4], antidepressant [5], anticonvulsant [6], and anti-tumor [7]. On the other hand, several studies have investigated pyrazolines as an effective inhibitor of the corrosion for different types of steel in acidic medium [8-11]. The aim of this work is the study of antioxidant and corrosion inhibition properties of two pyrazoline derivatives namely:

1-Formyl-3-phenyl-5-(4-methylphenyl)-2-pyrazoline P1 and 1-Formyl-3-phenyl-5-(4-chlorophenyl)-2-pyrazoline P2 (see Table 1), which were already synthetized and their inhibition efficiencies were predicted in our previous works [2, 12].

2. Materials and methods

The pyrazoline derivatives used in the present study were synthesized according to the procedure published in our recent artilces [2]. Both compounds contain several heteroatoms and aromatic rings, which motivated us to study their antioxidant and anticorrosion activities. Molecular structures, names and abbreviation of tested compounds are given in Table 1.

2.1. Determination of antioxidant activity

2.1.1. Antioxidant activity assay

Four complementary assays were selected to evaluate the antioxidant capacity of the synthesized compounds (P1 and P2) namely, DPPH scavenging activity [13], CUPRAC [14], ABTS cation radical Assay [15] and Superoxide radical scavenging assay [16]. MeOH was used as negative control while butylated hydroxyl toluene (BHT), butylated hydroxyl anisole (BHA) and α-Tocopherol were

used as positive controls. 96-well micro-plate reader (PerkinElmer, EnSpire Multimode Plate Reader, USA) was used to read out results of activites. The results were given as 50 % inhibition concentration (IC_{50}) or given as $A_{0.50}$, which corresponds to the concentration producing 0.500 absorbance.

2.1.2. Statistical analysis

The results are reported as mean value ± SD of three measurements. The IC_{50} and $A_{0.50}$ values were calculated by linear regression analysis, and one-way analysis of variance ANOVA to detect significant differences ($p < 0.05$) using XLSTAT.

2.2. Determination of anticorrosion activity

2.2.1. Material and solutions

Rectangular pieces with (1 cm × 1 cm × 0.5 cm) dimension of carbon steel (CS) with the following composition: 0.36 C, 0.66 Mn, 0.27 Si, 0.02 S, 0.015 P, 0.21 Cr, 0.02 Mo, 0.22 Cu, 0.06 Al and balance Fe, was used. Surface of CS specimens were polished with different grades of abrasive papers (SiC; 400-1200). The specimens were thoroughly washed with double distilled water, and dried at room temperature. The corrosive solution used is 1.0 M HCl.

2.2.2. Weight loss measurement

In order to investigate the effect of the present pyrazoline derivatives, weight loss measurement was performed according to ASTM G 31-72 standard method [17] in the concentration range of 10^{-4} M to 5×10^{-3} M at 298 K. The CS samples in triplicate were immersed in 1 M HCl with and without different concentrations of pyrazoline derivatives at 303 K for 6h. After that, the specimens were removed from the solutions, rinsed with water and absolute ethanol, finally dried and weighted. The corrosion rate (CR), the inhibition efficiency IEw (%) and the surface coverage (θ) were determined by using the following equations [18]:

$$C_R = \frac{\Delta m}{At} \dots (1)$$

$$IE_w(\%) = \frac{C_R^0 - C_R}{C_R^0} \times 100 \dots (2)$$

$$\theta = \frac{IE_W\%}{100} \dots (3)$$

Where, Δm is the weight loss of specimens, A is the surface area of CS pieces (cm^2) and t is the exposure time (h). C_R^0 and C_R are the corrosion rate values in the absence and presence of inhibitors, respectively.

3. Results and discussion

3.1. Antioxidant activity

The results of antioxidant activity are shown on Table 2 and expressed in terms of IC_{50} and $A_{0.50}$. The results of all antioxidant assays (Table 2) show that the P1 compound exhibits the highest antioxidant activity (IC_{50}: 75.97 ± 0.35, 189.64 ± 1.65, 34.39 ± 1.45 and 78.12 ± 1.39 µg/mL) compared to the other compound P2, but the two derivatives exhibited weak activity when compared their to the reference compounds. In the O_2^- DMSO alkaline assay the compound P1 showed closer activity to that of α-tocopherol (IC_{50}: 34.39 ± 1.45 and 31.52 ± 2.22µg/mL), respectively.

3.2. Anti-corrosion activity (weight loss measurement)

3.2.1. Effect of inhibitor concentration

The inhibition efficiency (IE_w%) and corrosion rate (CR) values obtained from weight loss method for different concentrations of inhibitors in 1M HCl at 298 K are presented in Table 3. Careful examination of the results showed that in the presence of inhibitors, the rate of corrosion decreases compared in the absence of inhibitors, with maximum of 94.73 % and 92.26 % at 5×10^{-3} M concentration of P1 and P2, respectively, representing an excellent inhibition performance of P1 compared to P2 towards the CS corrosion. These results can be attributed to the quick adsorption of pyrazoline derivatives on the CS surface, because of the presence of several reactive sites like heteroatoms (N and O), π-electrons and aromatic rings, which can greatly facilitate the adsorption of inhibitors onto the steel surface [18, 19].

3.2.2. Adsorption isotherm

In order to understand the mechanism of corrosion inhibitor and the type of interaction between the tested compounds (P1 and P2) and CS surface, various adsorption isotherms such as (Langmuir, Temkin, Freundlich) were employed to fit the experimental results. In our present study, the Langmuir adsorption isotherm, Eq. (4) [20], was found to be the most suitable mode to fit experimental data. The values of regression coefficients (R^2) were almost close to unity (via Table 4), which confirm that the adsorption of P1 and P2 on the CS surface obeys Langmuir isotherm model.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \dots (4)$$

Where C is the inhibitor concentration, θ is the surface coverage for different concentrations of inhibitor in 1M HCl and has been calculated from the weight loss measurement (eq. 3) and K_{ads} is the adsorption equilibrium constant. Fig 1 showed the plots of C/θ versus C for P1 and P2 at 298 K. The values of K_{ads} were calculated from the intercept of straight lines and listed in Table 4. The higher value of K_{ads} indicates that the inhibitors is strongly adsorbed on metal surface and follow the order P1 > P2.

The standard free energy of adsorption (ΔG°_{ads}) can be obtained by the following equation:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{\Delta G^{\circ}_{ads}}{RT}\right) \dots (5)$$

Where, 55.5 is the concentration of water in solution (mol/L), R is the gas constant (8.314 J K^{-1} mol^{-1}) and T is the absolute temperature (K). ΔG°_{ads} is reported in Table 4. The negative ΔG°_{ads} indicates that the adsorption is a spontaneous process, and reveals a strong interaction between the inhibitor molecule and the metal surface [21]. It was reported that the values of ΔG°_{ads} up to -20 $KJmol^{-1}$ are consistent with electrostatic interactions between the charged molecules and the charged metal (physisorption). While those more negative than -40 $KJmol^{-1}$ involve sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [18]. In our study, the values of ΔG°_{ads} obtained are between -20 kJ mol^{-1} and -40 kJ mol^{-1}, which means a mixed type of adsorption through physical and chemical adsorption. The results obtained from weight loss measurement confirm the theoretically predicted results in our previous work [12].

Table 1. Chemical names and structures of used compounds

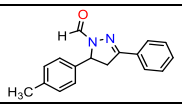
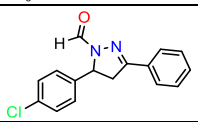
Name	Structure	Abbreviation
1-Formyl-3-phenyl-5-(4-methylphenyl)-2-pyrazoline		P1
1-Formyl-3-phenyl-5-(4-chlorophenyl)-2-pyrazoline		P2

Table 2. Antioxidant activity of the two compounds (P1 and P2) by the DPPH, CUPRAC, $ABTS^{+}$ and O_2^{-} DMSO alkaline assays[a]

Compounds	DPPH assay IC_{50} (µg/mL)*	ABTS+assay IC_{50} (µg/mL)*	$O2^{-}$ DMSO alkaline assay IC_{50} (µg/mL)*	CUPRAC assay $A_{0.50}$ (µg/mL)*
P1	178.28±0.35	328.10±1.81	81.69±2.35	>200
P2	75.97±0.24	189.64±1.65	34.39±1.45	78.12±1.39
BHA[b]	6.14±0.41	1.81±0.10	>200	6.62±0.05
BHT[b]	12.99±0.41	1.29±0.30	>200	8.97±3.94
α-Tocopherol[b]	13.02±5.17	7.59±0.53	31.52±2.22	19.92±1.46

*IC_{50} and $A_{0.50}$ values are defined as the concentration of 50% inhibition percentages and the concentration at 0.50 absorbance respectively. IC_{50} and $A_{0.50}$ were calculated by linear regression analysis and expressed as Mean±SD (n=3)

- [a]IC_{50} values represent the means ± SEM of three parallel measurements ($p< 0.05$)
- [b]Reference compound

Table 3. Weight loss data of CS in uninhibited and inhibited solutions at 298 K

Compounds	C (M)	CR (mg cm^{-2} h^{-1})	Θ	IEw(%)
P1	Blank	0.0969	-	-
	10^{-4}	0.0198	0.7957	79.57
	5.10^{-4}	0.0143	0.8524	85.24
	10^{-3}	0.0096	0.9001	90.01
	5.10^{-3}	0.0051	0.9474	94.73
P2	10^{-4}	0.0215	0.7781	77.81
	5.10^{-4}	0.0152	0.8431	84.31
	10^{-3}	0.0100	0.8968	89.68
	5.10^{-3}	0.0075	0.9226	92.26

Table 4. The adsorption parameters for the corrosion of CS in inhibited solutions at 298 K

Compounds	Slop	K_{ads} (M^{-1})	R^2	ΔG^{0}_{ads} (KJ Mol^{-1})
P1	1.09	30899	0.999	-35.57
P2	1.10	14512	0.999	-33.69

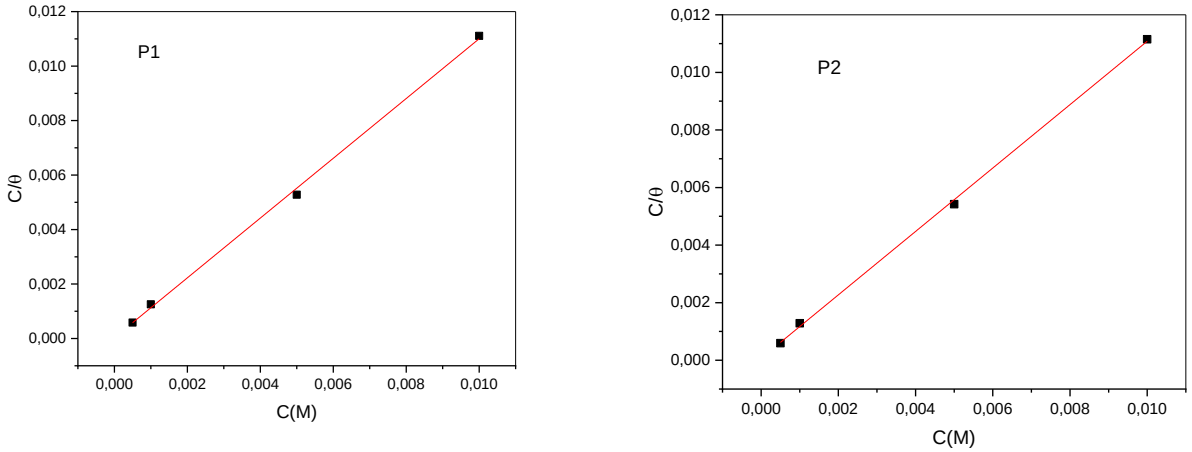


Figure 1: Plots of the Langmuir adsorption isotherm of inhibitors at 298 K

4. Conclusions

On the basis of the obtained results, the following conclusions have been drawn:

- This study showed that the synthetized pyrazoline compounds had a moderate antioxidant activity.
- The inhibition efficiency increases with increasing the P1 and P2 concentration, and the maximum inhibition efficiency reached 94 % and 92 % at 5.10^{-3} M Respectively.
- The adsorption of both inhibitors on the carbon steel surface obeys Langmuir adsorption isotherm, and occurred via both physical and chemical adsorption.
- The results obtained from weight loss study confirm the theoretical result (P1 > P2).

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