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Synthesis and application of new acetohydrazide derivatives as a corrosion inhibition of mild steel in acidic medium: Insight from electrochemical and theoretical studies

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ABSTRACT

Corrosion inhibition of mild steel in 15% HCl solutions by synthesized acetohydrazides namely, *N*′-[(1*Z*)-phenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (PQA) and *N*′-[(1*Z*)-4-chlorophenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (CPQA) was studied using chemical (weight loss) and electrochemical (potentiodynamic and electrochemical impedance spectroscopy) measurements. It was shown that PQA and CPQA act as good corrosion inhibitor for mild steel protection. It was concluded that the inhibition efficiencies increased with increase in the concentrations of the inhibitor. Tafel polarization studies showed that both the studied inhibitors act as mixed type inhibitor. The high inhibition efficiencies were attributed to the simple blocking effect by adsorption of inhibitor molecules on the steel surface. Atomic Force Microscope (AFM), Scanning Electron Microscope (SEM) and Energy Dispersion X-ray Spectroscopy (EDX) observations confirmed the existence of an absorbed protective film on the metal surface. The density functional theory (DFT) was employed for theoretical calculations and the obtained results were found to be consistent with the experimental findings.

1. Introduction

Acethydrazide is an important organic intermediate which is mainly used for the synthesis of nifuratrone in the pharmaceutical industry. Substituted pyrazolones can be prepared by treatment with corresponding hydrazide as strong alkalies [1] with hydrazide and its derivatives were used as versatile synthons. Hydrazides are found to be more reactive functional groups routinely used in protein and carbohydrate chemistry [2,3] and it is also reported that oligonucleotides can be modified with hydrazide [4].

Hydrochloric acid is widely used for pickling, cleaning and descaling of steel and ferrous alloys. The addition of corrosion inhibitors effectively secures the metal against an acid attack. Inhibitors are generally used in these processes to control metal dissolution. Most of the effective corrosion inhibitors are organic compounds containing nitrogen, oxygen, sulfur, aromatic rings and π-electrons in their structures [5–8]. The presence of atoms such as N, O and S in heterocyclic compounds determines both the efficiency and adsorption mechanism [9–14]. The molecular structure of these compounds plays an important role in determination of their inhibitive performance. Although, the protection mechanism of organic corrosion inhibitors has not been clearly understood [15], it is generally accepted that the corrosion inhibition is achieved due to the interactions between inhibitor molecules and the metal surface; resulting in formation of an inhibitive surface film [9,10,16,17]. The organic inhibitors decrease the corrosion rate by adsorbing on the metal surface and blocking the active sites by displacing water molecules and forming a compact barrier film on the metal surface. Most of the organic inhibitors are toxic, highly expensive and environment unfriendly. Research activities in recent times are geared towards developing the cheap, non-toxic and environment friendly corrosion inhibitors. A large number of organic compounds including heterocyclic compounds [18–23] were studied as corrosion inhibitors for mild steel [24–26].

The aim of this research is to study the corrosion inhibition effect of two synthesized compounds namely *N*′-[(1*Z*)-Phenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (PQA) and *N*′-[(1*Z*)-4-Chlorophenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (CPQA) on mild steel in 15% HCl solution by using weight loss measurement, electrochemical methods and theoretical calculations. Two derivatives of acetohydrazide have been chosen to discuss the effect of electron withdrawing (–Cl) substituent on inhibition efficiency of the inhibitor. To the best of our knowledge there is no any open literature pertaining on the studied compounds as a corrosion inhibitor on mild steel in

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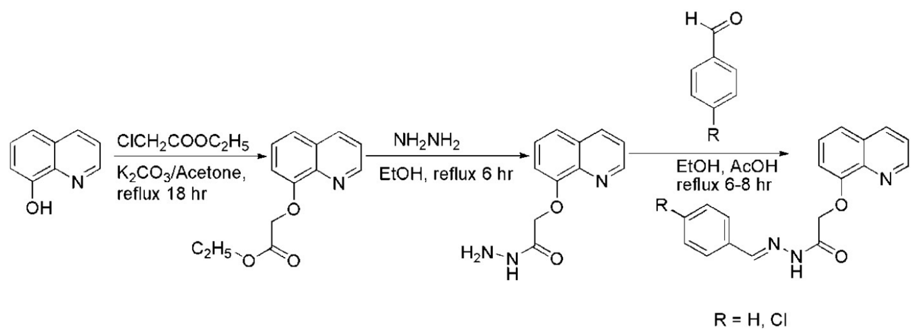

Scheme 1. Synthetic route of *N′*-[(1*Z*)-Phenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (PQA) and *N′*-[(1*Z*)-4-Chlorophenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (CPQA).

acidic medium. The present work is a continuation of our systematic studies on corrosion inhibitor of organic compounds [27–29].

2. Experimental

2.1. Synthesis of corrosion inhibitors

The compounds PQA and CPQA were synthesized by reported method [30] as shown in Scheme 1. The purity of the compound was checked by thin layer chromatography (TLC) and structure of the compounds was confirmed by using physic-chemical studies. The melting point, yield and IR data of the synthesized compounds are given below:

PQA: Yield 70%, m.p. 105 °C; IR (KBr) cm^{-1}: 3470 (N–H, CONH), 1674 (C = N), 1080 (C–O–C), 1181 (N–N), ^{1}H NMR (DMSO d6) δ: 8.17 (s, 1H, CONH), 7.61 (m, 11H, ArH), 7.41 (s, 1H, N = CH), 4.98 (s, 2H, OCH2); Anal. Calcd. for $C_{18}H_{15}N_3O_2$: C, 70.71; H, 4.84; N, 13.72. Found: C, 70.81; H, 4.92; N, 13.77%.

CPQA: Yield 70%, m.p. 132 °C; IR (KBr) cm^{-1}: 3455 (N–H, CONH), 1670 (C = O), 1624 (C = N), 1065 (C–O–C), 1188 (N–N), 754 (C–Cl); ^{1}H NMR (DMSO d6) δ: 8.25 (s, 1H, CONH), 7.41 (d, 2H, Ar–H near Cl), 7.11 (s, 1H, N = CH), 4.71 (s, 2H, OCH_2); Anal. Calcd. for $C_{18}H_{14}N_3O_2Cl$: C, 63.55; H, 4.07, N, 12.34. Found: C, 63.62; H, 4.12; N, 12.37%.

The structure of inhibitors namely: *N′*-[(1*Z*)-Phenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (PQA) and *N′*-[(1*Z*)-4-Chlorophenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (CPQA) are given in Fig. 1.

2.2. Material and methods

2.2.1. Mild steel samples

Mild steel specimens of size 6.0 cm × 2.5 cm × 0.1 cm and 1.0 cm × 1.0 cm × 0.1 cm with composition (w%) C, 0.14; Mn, 0.98; Si, 0.033; S, 0.018; P, 0.026; Cr, 0.02 and remainder iron were employed

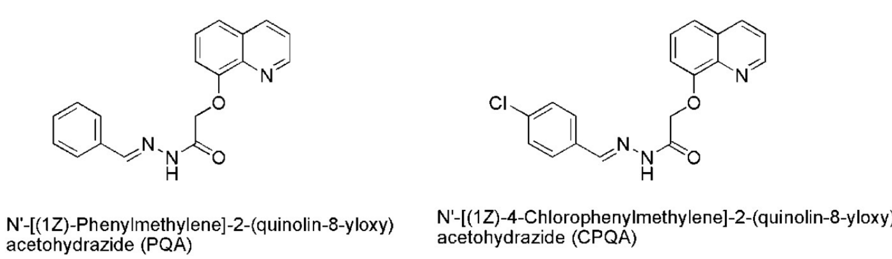

Fig. 1. Structure of *N′*-[(1*Z*)-Phenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (PQA) and *N′*-[(1*Z*)-4-Chlorophenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (CPQA).

Table 1
Corrosion parameters of mild steel in 15% HCl solution in the presence and absence of different inhibitors at different temperatures, obtained from weight loss measurements.

Conc. (ppm)	303 K			313 K			323 K			333 K		
	CR (mm y^{-1})	*θ*	*η*%	*CR* (mm y^{-1})	*θ*	*η*%	*CR* (mm y^{-1})	*θ*	*η*%	*CR* (mm y^{-1})	*θ*	*η*%
Blank	28.2	–	–	58.1	–	–	98.9	–	–	144.5	–	–
CPQA												
50	8.70	0.691	69.13	19.56	0.663	66.33	37.37	0.622	62.21	62.64	0.566	56.65
100	6.32	0.776	77.58	14.47	0.750	75.08	27.74	0.719	71.95	46.64	0.677	67.72
200	4.51	0.840	84.02	10.79	0.814	81.42	21.54	0.782	78.22	38.40	0.734	73.42
300	2.46	0.912	91.25	6.17	0.893	89.38	14.36	0.855	85.48	26.97	0.813	81.33
400	1.63	0.942	94.21	4.30	0.925	92.59	9.43	0.904	90.46	19.34	0.866	86.61
PQA												
50	7.75	0.725	72.52	17.59	0.697	69.72	33.55	0.660	66.07	57.84	0.599	59.9
100	5.62	0.800	80.06	12.94	0.777	77.72	25.81	0.739	73.90	44.69	0.691	69.07
200	3.42	0.887	87.84	8.15	0.859	85.97	17.70	0.821	82.10	32.97	0.772	77.18
300	1.88	0.933	93.32	5.17	0.911	91.10	12.98	0.867	86.87	24.53	0.830	83.02
400	1.35	0.952	95.18	3.50	0.939	93.97	9.17	0.907	90.72	17.80	0.876	87.68