ISSN: 0975-833X

Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 8, Issue, 08, pp.37002-37007, August, 2016

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

RESEARCH ARTICLE

STUDY OF SUBSTITUTED PYRAZOLE AND ITS DERIVATIVES AS ENVIORNMENTAL FRIENDLY CORROSION INHIBITOR FOR MILD STEEL IN ACIDIC MEDIUM

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ARTICLE INFO

Article History:
Received 27th May, 2016
Received in revised form
20th June, 2016
Accepted 07th July, 2016
Published online 31st August, 2016

Key words:

Pyrazole Derivatives,
Semicarbazide,
Acidic Medium,
Inhibition Efficiency,
Adsorption Isotherm,
Mild steel.

ABSTRACT

Aim of the present work is to synthesize 1-N amido 5-methyl 3(3-hydroxy) phenyl amino 1,2-pyrazole and its nitroso and benzoyl derivatives. Corrosion inhibition tendency of these compounds has been studied using weight loss method at different concentration of synthesized compounds at 30^0C in presence of HCl (0.1M) and H_2SO_4 (0.1M). Results of gravimetric analysis reveals that 1-N amido 5-methyl 3(3-hydroxy) phenyl amino 1, 2-pyrazole shows more corrosion inhibition efficiency towards H_2SO_4 as compared to HCl. Derivatives of these compounds also shows inhibition efficiency against corrosion of mild steel in acidic medium.

Citation: Priti Warbhe and Reshal Deshmukh, 2016. "Study of substituted pyrazole and its derivatives as enviornmental friendly corrosion inhibitor for mild steel in acidic medium", *International Journal of Current Research*, 8, (08), 37002-37007.

INTRODUCTION

Corrosion is an afflicting problem associated with industrial machinery or with use of metals. Corrosion is the deterioration of essential properties of a material due to reactions with its surrounding. Destruction of metals by corrosion results in high cost for maintenance and protection of metal. To avoid corrosion, use of inhibitory compounds is a best and economical method. Inhibitors reduce the corrosion of metallic parts of the machineries by retarding the rate of consumption and dissolution of metal in acidic medium (Francis *et al*., 2013; Aljourani *et al*., 2009). Literature survey proves that heterocyclic compounds containing N, O and S atoms are more active as corrosion inhibitor. Because N, O and S atoms and multiple bonds in these molecules facilitate to get adsorbed on the surface of the metal by physicochemical property of an inhibitor. Molecules that are planar have a greater tendency to adsorb at metal surface than molecule that has less planer geometry (Shukla *et al*., 2010; Ebenso *et al*., 2010; Al-Doori *et al*., 2014; Abdel Hameed *et al*., 2012; Rajappa *et al*., 2002)

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Pyrazoles are important member of heterocyclic compound which possess good corrosion inhibition efficiency against mild steel in acidic medium. Pyrazoles containing two N- atoms, one of which carries a pair of electron. These also show planer geometry (Ajay Kumar *et al*., 2013; Ezhilarasi *et al*., 2015; Ghodasara *et al*., 2014). Keeping in views, the difficulties because of corrosion faced by industrial field, economical loss and corrosion inhibitor properties of pyrazole, we will synthesize 1-N amido 5-methyl 3(3-hydroxy) phenyl amino 1, 2-pyrazole by condensation of primary amine, ethyl acetoacetate and semicarbazide. These compounds are non toxic, ecofriendly and follow the green chemistry route. The corrosion inhibitor properties of these compounds will be performed in presence of acids like HCl and H_2SO_4 (Herrag *et al*., 2008).

MATERIALS AND METHODS

All chemicals used for the synthesis were of analytical grade. The specimens are washed first with acid then thoroughly with double distilled water and dried with acetone and blower. The aggressive solutions (1M HCl and 1M H_2SO_4) was prepared by dilution of Analytical Grade 35.4 % HCl and 98% H_2SO_4 with double distilled water. Progress of all the reactions was

monitored by thin layer chromatography (TLC). The crude compounds were purified by recrystallization with ethanol. Mass spectra were also recorded. Melting points were determined by using Melting Point M-AB apparatus and were uncorrected. IR spectra were recorded by using AFFINITY Spectrophotometer. H NMR spectra were recorded on AVANCE II 400 NMR Spectrometer (Fouda *et al*., 2013; Praveen and, Venkatesha, 2009).

Analysis

Section A: Synthesis of 1-(N-phenyl-carboxamido)-propan-2-one (I) :-

An equimolar (0.01 mol) of the mixture of substituted primary amine 3- Aminophenol and ethyl acetoacetate in ethanol (99% pure ethanol) in 1:1 proportion was refluxed for 2-3 hrs in round bottom flask at 140^0C. The reaction mixture was cooled and poured onto crushed ice with continuous stirring. Resultant solid was filtered, washed thoroughly with cold water, dried and purified by ethanol to form **Ia**. Characteristics of these compounds are as follows

NMR:(Ia) Ar-H= δ (7.03 to 7.26ppm), NH= δ (9.21ppm), CH_2= δ (3.59ppm),-CH_3= δ (2.33ppm), OH= δ (11.27ppm)

Section B: Synthesis of 1-N amido 5-methyl 3(3-hydroxy) phenyl amino 1,2-pyrazole (II)

1-(N-phenyl-carboxamido)-propan-2-one (**Ia**) (0.01M) was then refluxed with semicarbazide (0.01M) in ethanol as a solvent for 2-3 hrs. After refluxing the reaction mixture was allowed to distil off. A shiny crystal of pyrazoles **(IIa)** is obtained. These were recrystallised with ethanol. It shows following properties.

Elemental Analysis: Obv (Cal) : C = 54.67 (56.89) , H = 4.19 (5.17) , N = 25.12 (24.13) , O = 11.45 (13.79)

- The elemental analysis indicated the molecular formula of product as $C_{11}H_{12}N_4O_2$.
- The compound was white crystalline solid with melting point 294^0C
- It is insoluble in water but soluble in organic solvent.
- It gives positive test for Nitrogen.
- IR Analysis : The IR of (IIa) (Fig.1) Showed absorption band for-
- NMR Analysis : Ar-H=δ(6.53 to 7.82ppm), NH=δ(8.90ppm), CH= δ(3.48ppm),-CH_3=δ(2.54ppm), OH=δ(8.08ppm), NH_2 = δ(6.12ppm)

Section C: Synthesis of Nitroso derivative of 1-N amido 5-methyl 3(3-hydroxy) phenyl amino 1,2-pyrazole (III)

1-N amido 5-methyl 3(3-hydroxy) phenyl amino 1,2-pyrazole (II) was mixed with conc. HCl. Cool this solution at 0-5° C. To this acidic solution 5ml of 20% sodium nitrite was added with continuous stirring. The reaction mixture was allowed to stand for half an hrs for completion of reaction. It was filtered through Buchner funnel and washed with water (Kasimogullari *et al*., 2010; Das *et al*., 2008). Recrystalised with ethanol to form **III**. Physical characteristics were shown in Table 1.

Absorption observed (cm-1)	Assignment	Literature value (cm-1)
3154.71	N-H Stretching	3400-3100
1537	C=N Stretching	1689-1471
1287.54	C-N Stretching	1350-1280
1156.37	N-N Stretching	1202

Section D : Synthesis of Benzoyl derivative of 1-N amido 5-methyl 3(3-hydroxy) phenyl amino 1,2-pyrazole (IV)

1-N amido 5-methyl 3(3-hydroxy) phenyl amino) 1,2-pyrazole (II) was mixed with NaOH solution.

The reaction mixture was cooled on ice bath. Approximately 2ml Benzoyl Chloride was added drop wise and shake. Allow the reaction mixture to settle down. Filter the mixture (Okafor et al., 2004; Hassan et al., 2014). Recrystallised with ethanol to form **IV**. Physical characteristics were shown in Table 1.

Section E: Determination of Inhibition Efficiency

Specimen Preparation

Commercially available steel sheet (weight= 5 gm) was used for experiment. The sheets were cleaned by scrubbing with sandpaper and washed under the flow of water and degreased in absolute ethanol. They were then dried in acetone and weighed accurately.

Sample Preparation

0.001M, 0.002M, 0.004M,0.006M, 0.008M, 0.01M solution of compounds were prepared in 50ml 0.1M HCl and 0.1M H_2SO_4. Accurately weighed specimen of steel was placed in a sample prepared above. Maintain the temperature at 30^0C.

After 8 hours specimen sheet placed out, dried properly and weighed (Sharma *et al*., 2009; Pathak and Kushwah, 2014).

Weight correction (CR) and corrosion inhibition efficiency (%IE) (5) can determined by the formula

CR = Wb - Wi
%IE = {(Wb – Wi) / Wb} X 100
Where: CR = Weight Correction,
%IE = Corrosion inhibition efficiency,
Wb = Weight of steel specimen in absence of inhibitor,
Wi = Weight of steel specimen in presence of inhibitor.

RESULTS

Physical and elemental analysis of 1-N amido 5-methyl 3(3-hydroxy) phenyl amino) 1,2-pyrazole (II) and its derivatives (III and IV) confirms the formation of pyrazoles. These pyrazoles are used as corrosion inhibitor for mild steel in presence of HCl and H_2SO_4. Results of corrosion inhibition at different concentration are shown in Table 1 and Table 2.

Table I. Physical characteristics of Nitroso and Benzoyl Derivative of 1-N amido 5-methyl 3(3-hydroxy) phenyl amino 1,2-pyrazole

S.No.	Compound Name	Derivative Name	Mol. Formula	MP (°C)	Elemental analysis obs (cal)			
					C	**H**	**N**	**O**
1	1-N amido 5-methyl 3[3-hydroxy] phenyl amino] 1,2-pyrazole (II)	1-N [Nitro amido] 5-methyl 3[3-hydroxy] phenyl amino] 1,2-pyrazole (III)	$C_{10}H_{10}N_4O_2$	120	49.23 (55.04)	4.65 (4.58)	22.96 (25.68)	18.97 (14.67)
2	1-N amido 5-methyl 3[3-hydroxy] phenyl amino] 1,2-pyrazole (II)	1-N[Benzoyl amido] 5-methyl 3[3-hydroxy] phenyl amino] 1,2-pyrazole (IV)	$C_{17}H_{16}N_3O_2$	> 300	62.68 (69.38)	4.25 (5.44)	18.46 (14.28)	17.15 (10.88)

Reaction scheme

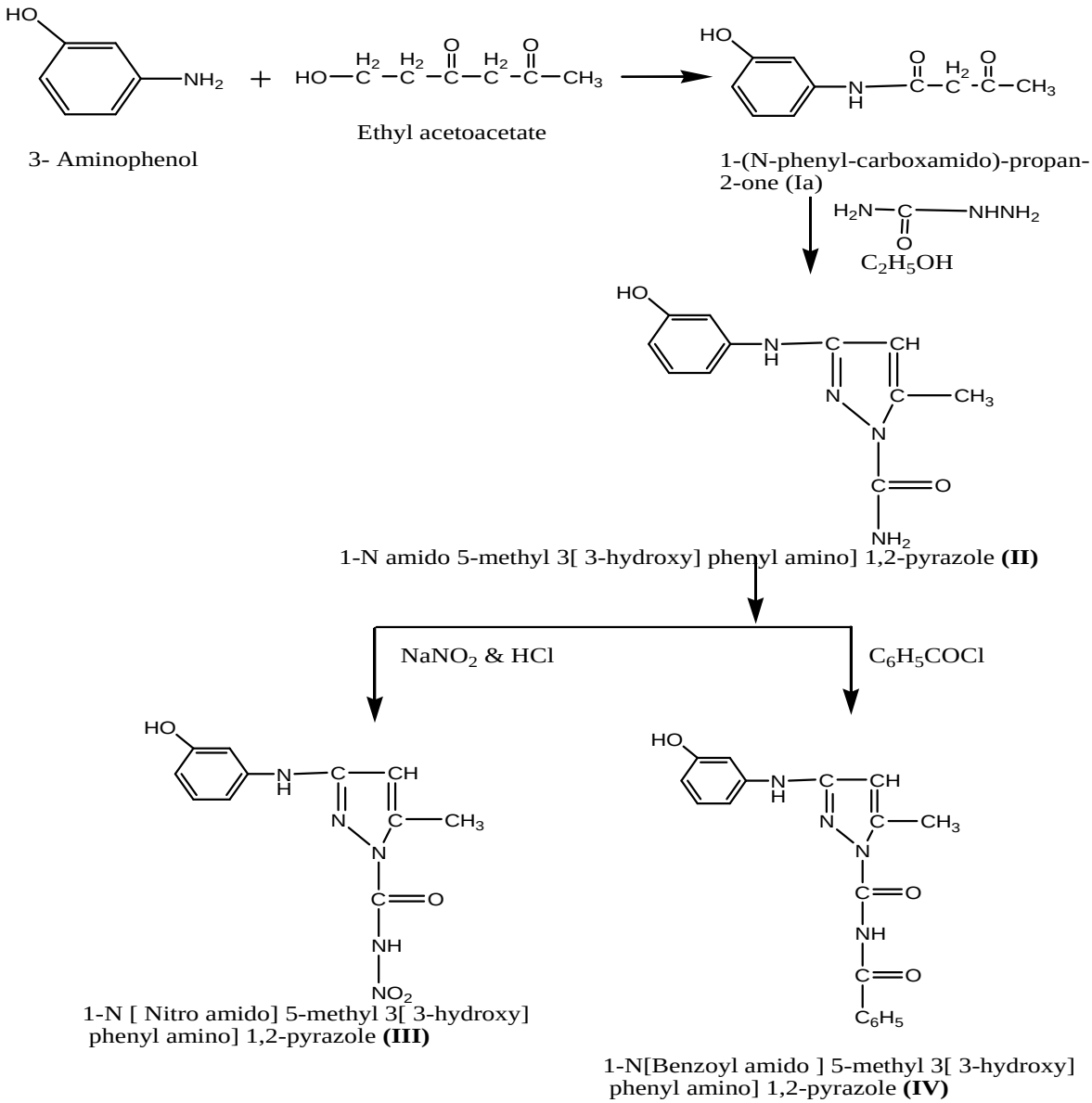

Table II: Corrosion Inhibition of 1-N amido 5-methyl 3[3-hydroxy] phenyl amino] 1,2-pyrazole (II) at different concentration

CONC	HCl		H_2SO_4	
	CR	**%E**	**CR**	**%E**
0.001M	54	45	65	49
0.002M	90	49	114	52
0.004M	220	55	215	57
0.006M	284	58	336	59
0.008M	584	67	620	66
0.01M	720	70	963	71

Table III. Corrosion Inhibition of Derivatives of 1-N amido 5-methyl 3[3-hydroxy] phenyl amino] 1, 2-pyrazole (III and IV) at different concentration

CONC	Nitroso Derivative of Pyrazole				Benzoyl Derivative of Pyrazole			
	HCl		H_2SO_4		HCl		H_2SO_4	
	CR	%E	CR	%E	CR	%E	CR	%E
0.001M	59	50	70	53	40	31	57	42
0.002M	98	54	121	55	77	40	102	48
0.004M	232	59	222	59	108	52	197	53
0.006M	302	61	349	62	187	54	278	59
0.008M	502	70	434	67	345	59	396	64
0.01M	638	72	678	72	428	65	613	68

Graphically these results were represented as

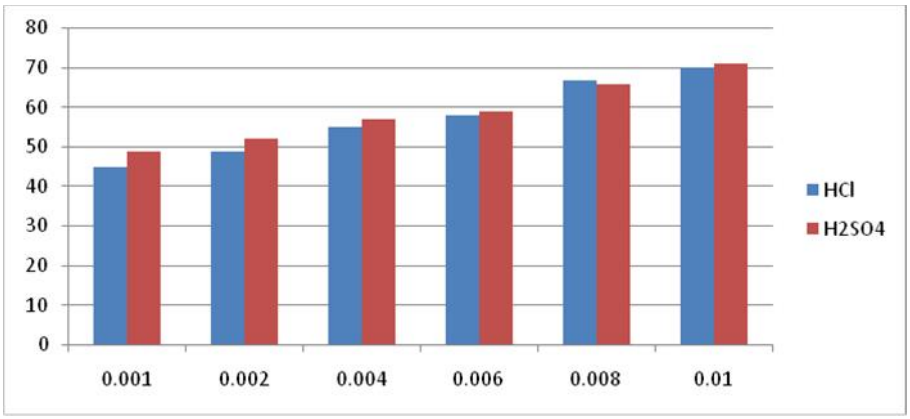

Fig. 1. Graphical representation of 1-N amido 5-methyl 3[3-hydroxy] phenyl amino] 1,2-pyrazole (II) at different concentration

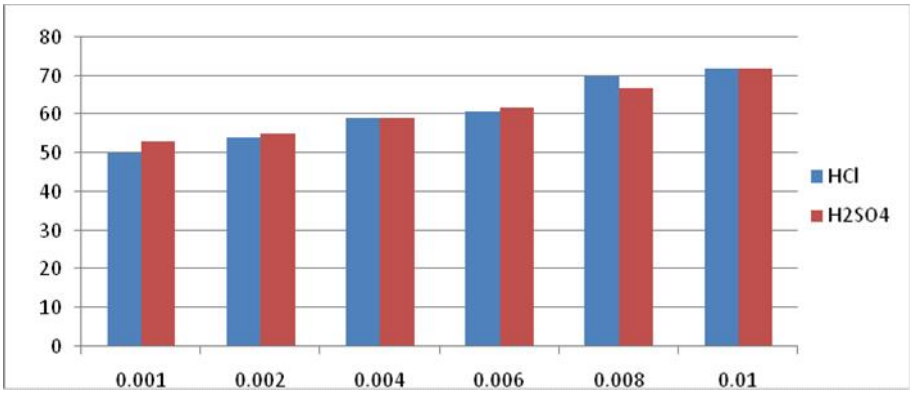

Fig. 2. Graphical representation of 1-N [Nitro amido] 5-methyl 3[3-hydroxy] phenyl amino] 1,2-pyrazole (III)

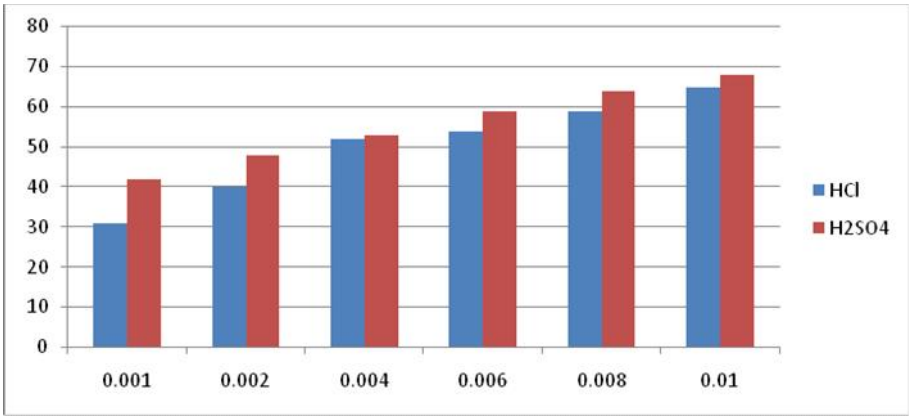

Fig. 3. Graphical representation of 1-N [Benzoyl amido] 5-methyl 3[3-hydroxy] phenyl amino] 1,2-pyrazole (IV)

DISCUSSION

The results of corrosion rate and inhibition efficiency that obtained from weight loss measurement technique at different concentration of 1-N amido 5-methyl 3(3-hydroxy) phenyl amino) 1, 2-pyrazole (II) and its derivatives after 8hrs at 30^0C , indicate that corrosion rate of mild steel reduces by use of inhibitors in acidic medium. Rate of corrosion in H_2SO_4 is remarkably reduced. When steel specimen placed in acidic medium without inhibitor, the decrease in weight of mild steel specimen after 8 hrs was more. When inhibitor was added it will get adsorbed on the surface of the steel which makes impediment towards corrosive environment. The increase in corrosion efficiency with increase in concentration of inhibitor indicates that more inhibitor molecules are adsorbed on the metal surface.

Conclusion

- Results obtained from the experimental data shows that 1-N amido 5-methyl 3(3-hydroxy) phenyl amino) 1,2-pyrazole was a good inhibitor of steel in HCl and H_2SO_4 .
- 1-N amido 5-methyl 3(3-hydroxy) phenyl amino) 1, 2-pyrazole shows more inhibition efficiency against H_2SO_4 as compared to HCl with varied concentration**.**
- Inhibitor efficiency of 1-N (Nitro amido) 5-methyl 3(3-hydroxy) phenyl amino) 1,2-pyrazole (III) was high while that of 1-N(Benzoyl amido) 5-methyl 3(3-hydroxy) phenyl amino) 1,2-pyrazole (IV) was less.
- As the concentration of the inhibitory compound increases the corrosion inhibition efficiency also gets increased.

Acknowledgements

The authors are sincerely thankful to the Principal Science College, Nagpur, India for providing laboratory facilities and the Head SAIF, Chandigarh, India for providing IR, H1NMR, Mass, UV spectroscopic facility. The authors are also grateful to the Head of Reliable Analytical Laboratory, Science College, Nagpur, India for carrying out analytical work.

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