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N-[AMIDO] Substituted Pyrazole Compound used as Corrosive Inhibitor for Mild Steel in Acidic Environment

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Abstract

The corrosion of metals and alloys in acidic medium is a world-wide scientific problem as it affects the various processes like metallurgical, chemical and oil industries. Thus, an inhibition action of 1-N amido 3-methyl 4[2-methoxy] phenyl amino 1, 2-pyrazole on corrosion of steel in acidic medium has been investigated by weight loss method. Result obtained reveals that presence of these compounds reduces corrosion rate. Corrosion action increases with the increase in concentration of pyrazoles compounds. The increase in temperature leads to decrease in the inhibition efficiency of the compounds.

Keywords: Corrosion inhibition, pyrazoles and its derivatives, gravimetric analysis, acid medium, Inhibition efficiency.

Introduction

Corrosion is a process of destruction of metal and alloys either by environmental conditions or human activities mostly in industrial field. It changes the original composition of metal or removes the scales. Thus in industries corrosion results in highly cost for maintenance and protection of materials used[1,2]. Therefore, an idea of use of inhibitors arises rapidly. Various organic compounds reduce the corrosion of metallic materials by controlling the metal dissolution and consumption[3-5].

Heterocyclic compounds containing N atoms plays important role in corrosion inhibitors. Corrosion inhibitors are the substances which reduces rate of destruction of metals and alloys[6,7]. Important structural feature of these heteroatom are the planar electrons and lone pair of electrons present on the heteroatom that affect on the adsorption of these molecules on the metal surface[8,9]. Pyrazoles are important class of heterocyclic compounds. It contains two nitrogen atoms, one is basic and other is neutral in nature[10]. Therefore pyrazoles are useful in field of medicinal chemistry, organic chemistry, pharmaceutical chemistry, industrial chemistry, petroleum engineering etc. Beside this, pyrazoles are used as corrosion inhibitors for metals and alloys like iron, aluminium, copper, mild steel etc[11].

Various metals and alloys are widely used in many applications such as pharmaceutical industry, thermal power plant, desalination plants, construction materials, chemical cleaning and pickling process, due to their stability, good corrosion resistance, high strength, workability and weldability. Acidic solutions are extensively used in chemical laboratories and in several industrial processes such as acid pickling, acid cleaning, acid rescaling and oil wet cleaning etc. Due to presence of acidic medium, metals or alloys undergoes corrosion and detoriate the metal surfaces[12,13].

Use of inhibitors is one of the most practical methods for protection of metals and alloys against corrosion, especially in acid solutions, to prevent metal dissolution and acid consumption[14]. The present study aimed to test newly synthesized compound 1-N amido 3-methyl 4 [2-methoxy] phenyl amino 1, 2-pyrazole as a corrosion inhibitor in acidic medium at different concentration of HCl and temperature. This property was evaluated by weight loss method[15,16].

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 solution (1M HCl) was prepared by dilution of Analytical Grade 35.4 % HCl with double-distilled water. IR spectra were recorded by using AFFINITY-1 FTIR Spectrophotometer. H NMR spectra were recorded on AVANCE II 400 NMR Spectrometer. Melting points were determined by using Melting Point M-AB-92 apparatus and were uncorrected. 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.

Experimental: Section A: Synthesis of 1-(N-phenyl-carboxamido)-propan-2-one: An equimolar (0.01 mol) of the mixture of substituted primary amine and ethyl acetoacetate in ethanol (99% pure ethanol) in 1:1 proportion was refluxed for 6-8 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), OCH_3=δ(3.87ppm)

Section B: Synthesis of 1-N amido 3-methyl 4[2-methoxy] phenyl amino 1, 2-pyrazole: 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. Similarly compounds were synthesised. NMR: [IIa] Ar–H=δ (6.93 to 7.82 ppm), NH=δ (9.03 ppm), CH=δ (3.36ppm), $-CH_3$=δ (2.69ppm), OCH_3=δ (3.23ppm), NH_2 = δ (4.97ppm)

Section C: Weight loss measurement technique: Specimen Preparation: Commercially available steel sheet (weight=5 gm) was used for experiment. The sheets were cleaned by scrubbing with sand paper and washed under the flow of water and degreased in absolute ethanol. They were then dried in acetone and weighed accurately.

Sample Preparation: 1 mg of above compound is weighed and adds in a beaker (100ml capacity) containing 50ml 0.1M HCl. Same procedure was applied for 0.05M, 0.01M, 0.005M, 0.001M HCl.

Accurately weighed specimen of steel was placed in a sample prepared above. Maintain the temperature at 30^0C. After interval of 60 min specimen sheets placed out, dried properly and weighed. Place it again in the same beaker. Same procedure was repeated at 50^0C.

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

$CR = W_b - W_i$

$\% IE = \{(W_b - W_{i)} / W_b\} X 100$

Where: CR = Weight Correction, %IE = Corrosion inhibition efficiency, W_b = Weight of steel specimen in absence of inhibitor, W_i = Weight of steel specimen in presence of inhibitor.

Results and Discussion

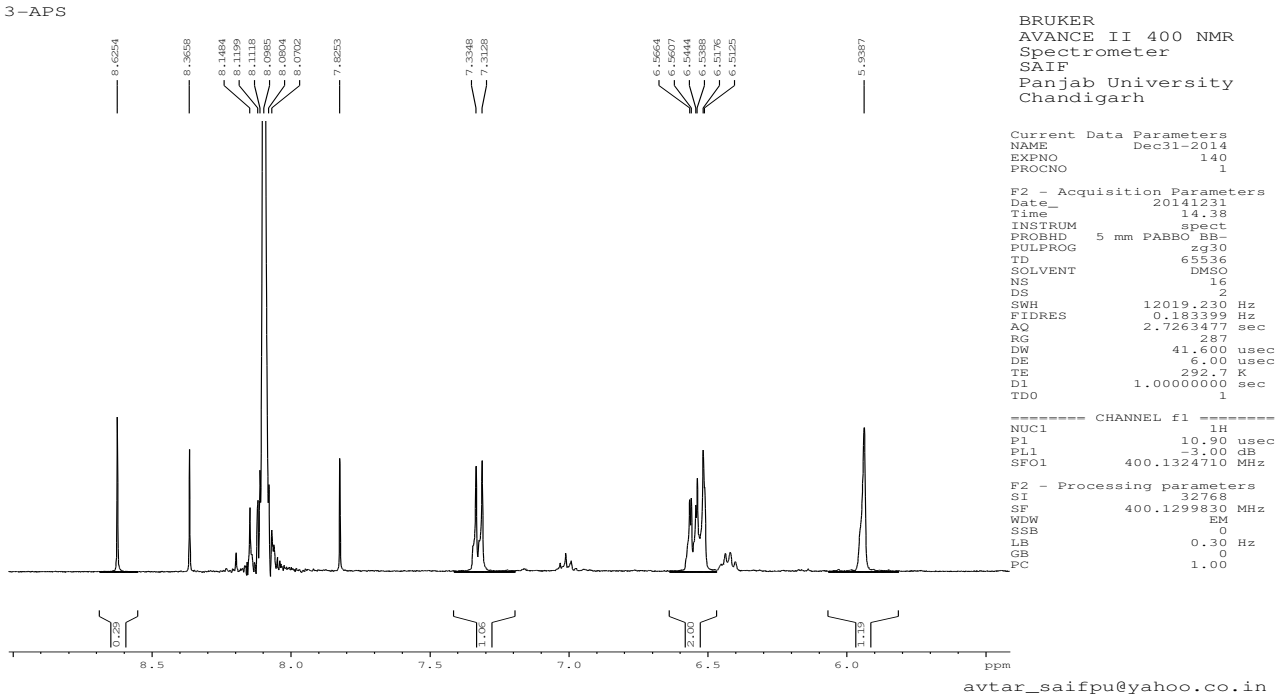
As shown in Table-1 and Table-2, gravimetric analysis result of 1-N amido 3-methyl 4[2-methoxy] phenyl amino 1,2-pyrazole for different concentration of Hl at 30^0C and 50^0C shows the weight loss of steel specimen. The inhibitory activity of compound is because of presence of C, N, O atoms. These atoms form a protective layer on the surface of the steel which reduces rate of corrosion. The presence of lone pair of electron helps to the electron transfer from the inhibitor to the steel, forming a co-ordinate covalent bond. Multiple double bonds also form a greater physical adsorption. Graphs will plot Time in min Vs weight loss in mg as shown in Figure-1 and Figure-2.

Table-1
Gravimetric results of Compound IIa at different concentration of HCl after each hour at 30^0C

Conc of HCl	60 min		120 min		180 min		240 min	
	CR	% IE	CR	% IE	CR	% IE	CR	% IE
0.001M	74	75%	135	68 %	221	62%	369	58%
0.005M	106	61%	134	47%	238	49%	351	46%
0.01M	144	62%	219	60%	283	56%	364	55%
0.05M	196	60%	323	60%	543	56%	520	54%
0.1M	360	63%	417	57%	530	56%	681	54%

Table-2
Gravimetric results of Compound IIa at different concentration of HCl after each hour at 50^0C

Conc of HCl	60 min		120 min		180 min		240 min	
	CR	% IE	CR	% IE	CR	% IE	CR	% IE
0.001M	101	70%	152	63 %	262	61%	445	59%
0.005M	180	69%	265	68%	358	64%	546	60%
0.01M	238	68%	363	69%	409	55%	558	59%
0.05M	362	68%	494	63%	560	59%	597	45%
0.1M	617	63%	633	67%	634	48%	775	50%



NMR spectra of 1-N amido 3-methyl 4[2-methoxy] phenyl amino 1, 2-pyrazole

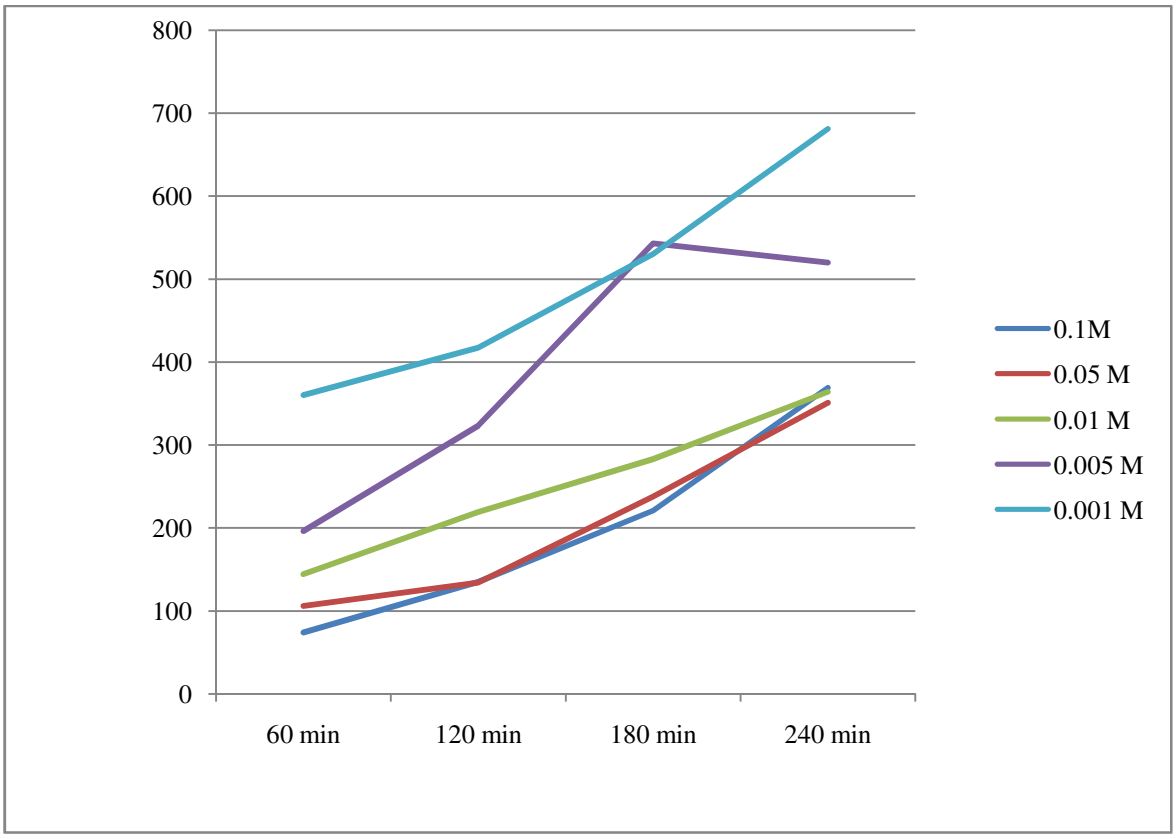


Figure-1
Graphical representation of corrosion inhibition at 30^0C

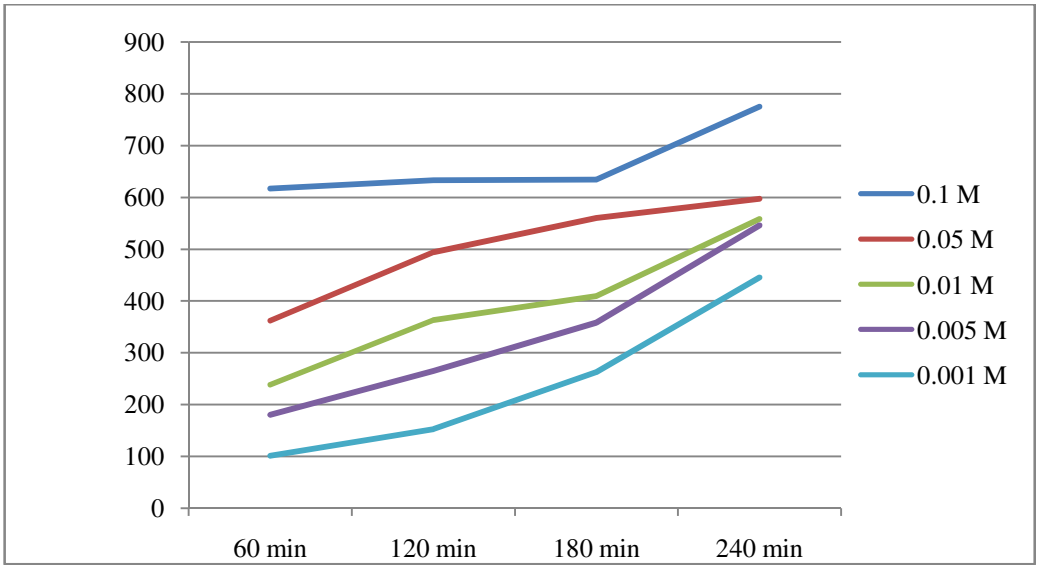


Figure-2
Graphical representation of corrosion inhibition at 50^0C

Conclusion

From result it was conclude that the addition of compound 1-N amido 3-methyl 4[2-methoxy] phenyl amino 1, 2-pyrazole reduces the rate of corrosion at different concentration of HCl. The rate of corrosion increased with increasing temperature with presence and absence of inhibitor. Hence, rate of corrosion affected by change in concentration of acidic medium and temperature also.

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