A study of synthesized mannich base inhibition on mild steel corrosion in acid medium

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ABSTRACT

Mannich base was synthesized and characterized using FT-IR. H^1NMR, 2D NMR, C^{13} NMR and Mass spectral studies and it was tested as a corrosion inhibitor for mild steel in 5% HCl solution using weight loss method over the temperature range of 303 – 353K. The inhibition efficiency was increased with respect to concentration of inhibitor and decreased with respect to temperature in 5% HCl at constant immerse time 30 minutes.

Keywords: Mild steel HCl and Mannich bases.

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INTRODUCTION

Mild steel corrosion is one of the major issues in many chemical industries because of the increasing usage of mild steel and inorganic acids in chemical industries. One of the best methods to control mild steel corrosion is using organic inhibitors. Acid inhibitors are usually used in several industrial processes to control the corrosion of metals. Most of the well-known acid inhibitors used are organic compounds containing nitrogen, sulphur and oxygen atoms. These compounds are strongly adsorbed on mild steel surface by forming a co-ordinate bond between the unpaired electrons present on nitrogen, sulphur and oxygen atoms and vacant d-orbitals in mild steel. [1-2]The mannich reaction is a three component condensation reaction in which an active H atom(substrate) is allowed to react with an aldehyde or ketone and primary or secondary amine, concomitant release of water to produce a new base known as a Mannich base.[3-4] The synthetic utility of Mannich reaction is evident from its application in the synthesis of many natural products and biologically important compounds.[5-8] such as antitubercular, antimalarial, analgesic drugs.[9-10] has been reported 1((Cyclohexylamino)methyl)urea exhibit potent corrosion inhibitor.

The adsorption of the inhibitors on the metal surface, decreases the corrosion rate. The most efficient inhibitors are compounds containing π bonds. The adsorption of these compounds is influenced by the electronic structures of inhibiting molecules, steric factor, aromaticity, electron density at the donor site, molecular area and molecular weight of the inhibitor. Compounds having functional groups such as –CHO, -CO, -N=N and R-OH also act as good anticorrosive inhibitore.[11] In the present study the inhibition potential of the Mannich base of (PABU) in 5% hydrochloric acid have been investigated.

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MATERIALS AND METHODS

All reagents were commercially available and used without further purification. Solvents were distilled from appropriate drying agents subsequently prior to use. The C, H and N were analyzed on a carlo – Erba 1106 elemental analyzer. IR spectra were recorded on a shimadzus FTIR affinity 1 spectrophotometer in KBrall melting points were taken in open capillary tubes in ^{o}C by using richerkjung Heizbank melting point apparatus, Ultraviolet – visible (UV – Vis) absorption spectra were recorded on a Perkin-Elmer Lambda 35 spectrophotometer at the wavelength of maximum absorption (λ_{max})in DMSO at room temperature. Raman spectra were Recorded on Bruker RFS 27, ^{1}HNMR, ^{13}C NMR and 2d NMR spectra were recorded on a Bruker Advance DPX 400 MH$_Z$ ultra-shield FT –NMR spectrophotometer in DMSO-d$_6$ with TMS as internal standard chemical shifts are expressed in (б units ppm). SAIF IIT Madras-36. The mass spectral studies were recorded on JEOL D - 300 (EI) mass spectrometer.

2.Experimental

2.1 Synthesis of Mannich base

PABU was synthesized by employing the Mannich synthetic route. To the aqueous solution of urea (0.6 g, 0.01 mol), ethanolic solution of 4-chlorobenzaldehyde (0.9412g, 0.01 mol), was added, followed by 4-amminopyridine (1.4057g, 0.01 mol) with constant stirring at room temperature, for about 3h. The solid began to separate after 2h. After 10 days the hard cake obtained was washed with distilled water several times and finally with a small amount of acetone, dried in air and then kept at 70°C in an air oven. The compound was recrystallized from methanol. The yield of the compound was found to be 90%. The compound is a creamy white solid and decomposes at 102 ^{o}C. It is insoluble in water, partially soluble in carbon tetrachloride and methanol. It is insoluble in dimethylsulfoxide and dimethylforamide (Manjula, 2009)

Scheme

1-[(4-chlorophenyl)(pyridin-4-ylamino)methyl]urea
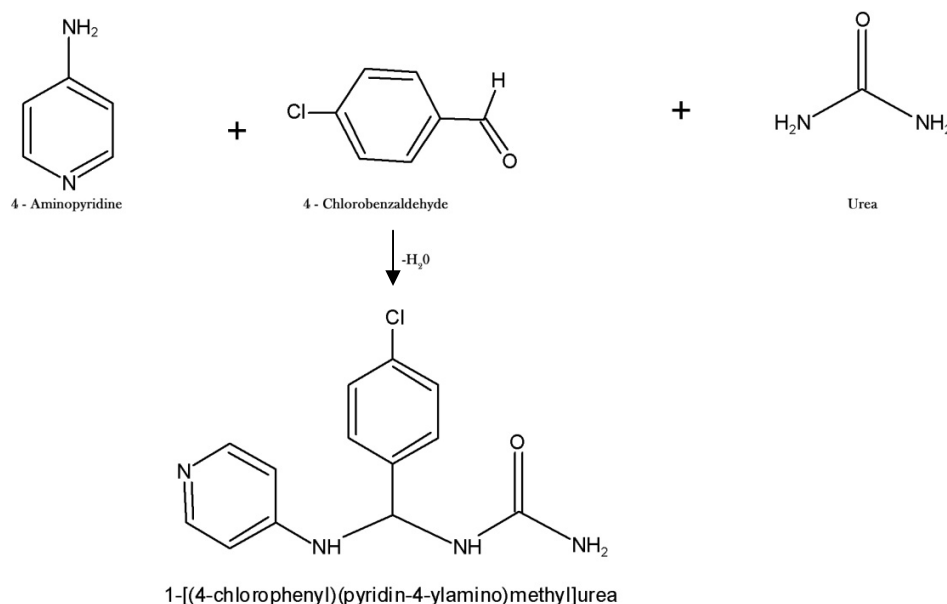
Spectral data

M.F: C$_{13}$ H$_{13}$ ClN$_4$O yield 90% m.p 100-102°C, Mol.wt: 277. FTIR KBr ν in cm^{-1}: 3426 (-NH), 3206, 2973 (CH aromatic and aliphatic), 1704 (C=O), 1599 (δ NH), 1158, 1061 (C-N-C) 988 (Pyridine ring breathing mode), 800 (CH opb of pyridine and benzene ring), 703 δ NH (Wagging and twisting), 526 (δ O-C-N). FT Raman polycrystalline powder ν in cm^{-1}: 3058 (-NH), 3029, 2916 (CH aromatic and aliphatic), 1160, 1090 (ν C-N-C), 846 (CH opb of pyridine and benzene ring), 115, 88 (Skeletal bending vibration). ^{1}H NMR (400 MHz, DMSO d$_6$), δ 9.99 (S,NH), δ 8.04-8.02 (d, NH), δ 7.94 – 7.91 (d, NH$_2$), δ 7.70-7.30 (m, 4H Phenyl ring), δ 6.58-6.02 (m, 4H pyridine ring), δ 5.99 (S, CH) ^{13}C NMR (400 MHz, DMSO d$_6$), δ 160.29 (S, 1C C=O), δ 158.20 (S, 1C), δ 152.45 (S, 2C), δ

109.3 – 108.6 (S, 2C), δ 154.78 (S, 1C), δ 149.86 – 149.72 (S, 1C), δ 128.85 (S, 2C), δ 132.81 (S, 2C), 2D NMR (400 MHz,DMSO d_6). The ^1H – ^1H and ^1H – ^{13}C correlation of PABU (fig 1). Which shows the better results corresponding to the those of ^1HNMR and $^{13}CNMR$ spectral data. The 2d NMR spectral study of the (PABU) substantiates the ^1HNMR and $^{13}CNMR$ spectral assignment. FAB Mass (Positive mode) m/z: 277 ($C_{13}H_{13}ClN_4O$), base peak m/z: 218 ($C_{12}H_{10}ClN_2^+$),m/z: 139 ($C_7H_6ClN^+$), m/z:112 ($C_7H_5Cl^+$) m/z: 79 ($C_5H_5N^+$). Calculate: C 40.62% N 12.50% O 3.12%. Found: C 40.60% H 40.61% N 12.48% O 3.10 %.

Figure.1
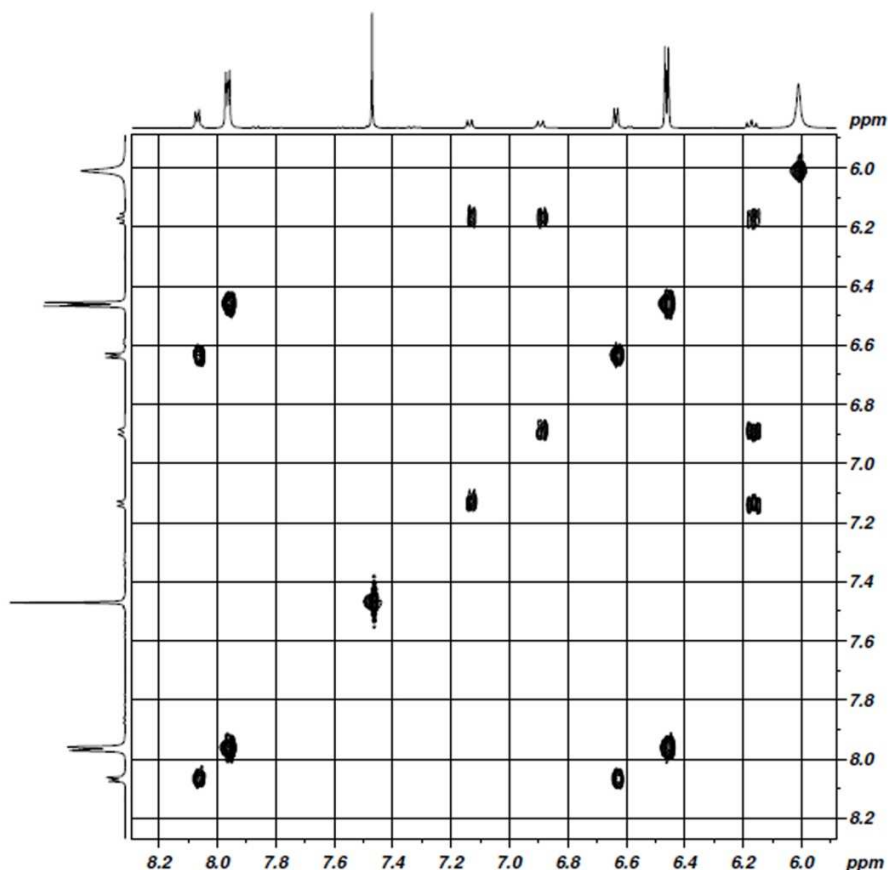
2D NMR spectrum of PABU

2.2 Specimen preparation
Mild steel plates were used in this study, having a composition of Mn: 0.01%, Cu: 0.02%, Si: 0.02%, P: 0.02%, C: 0.08%, and Fe: 99.75%. The specimens of dimension 4 cm×1.5 cm×0.15 cm are used. The specimens were polished using 1/0, 2/0, 3/0, and 4/0 grade emery papers and finally degreased with acetone and immediately used for experiments.

2.3 Corrosion monitoring technique
2.3.1 Weight loss method
The 5% hydrochloric acid are prepared by using distilled water in 100 mL standard flasks. Weight loss measurements were carried out by weighing the specimens before and after immersion in 100mL acid solution for 30 min in the absence and presence of inhibitors at various inhibitor concentrations. From the initial and final mass of the specimen, the weight loss was calculated. From this weight loss value, inhibition efficiency (IE) and corrosion rate were determined.

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IE has been determined by the following relationship[12]

Inhibition Efficiency (%) = [$(W_b - W_i)/W_b$] × 100

Where W_b and W_i are the weight loss without and with inhibitor.

The corrosion rate has been determined by the relationship (Ambrish et al., 2010):

Corrosion rate (mmpy) = (87.6×W)/(A×T×D)

Where W is the weight loss in mg; A is the area in cm^2; T is the time of immersion in hours and D is the density in g cm^{-3}.

Table 1.1 variation of IE in 5% HCl with 30 min at 303K

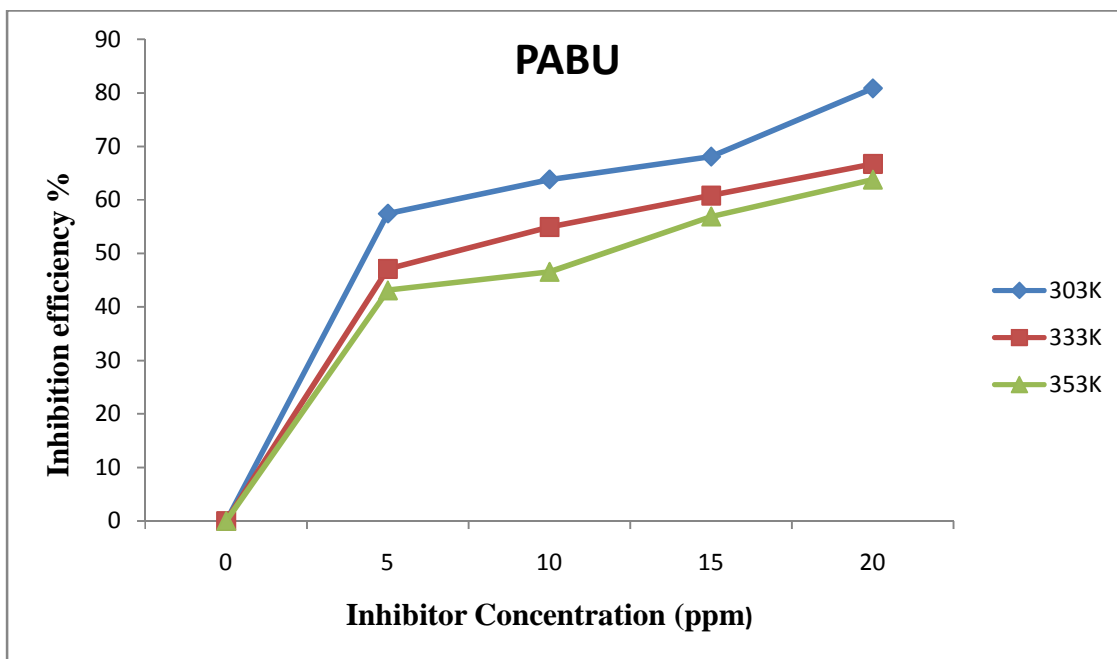| Conc. of inhibitor(ppm)	Weight loss(mg)	Corrosion rate(mmpy)	IE(%)
00	0.0047	0.0149	-
05	0.0020	0.0063	57.44
10	0.0017	0.0054	63.82
15	0.0015	0.0048	68.08
20	0.0009	0.0029	80.85

Figure.3 Variation of IE with various concentration of inhibitors at different temperature for 30mins

Table 1.2 variation of IE in 5% HCl with 30 min at 333K

Conc. of inhibitor(ppm)	Weight loss(mg)	Corrosion rate(mmpy)	IE(%)
00	0.0051	0.0162	-
05	0.0027	0.0086	47.05
10	0.0023	0.0073	54.90
15	0.0020	0.0063	60.78
20	0.0017	0.0054	66.67

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Table 1.3 variation of IE in 5% HCl with 30 min at 353K

Conc. of inhibitor(ppm)	Weight loss(mg)	Corrosion rate(mmpy)	IE(%)
00	0.0058	0.0184	-
05	0.0033	0.0105	43.10
10	0.0031	0.0098	46.55
15	0.0025	0.0079	56.89
20	0.0020	0.0063	63.79

RESULTS AND DISCUSSION

3.1 Weight loss method

Tables 1.1-1.3 and Fig.3 represent the IE of the inhibitor as a function of different temperature and different inhibitor concentrations at constant time and constant concentration of hydrochloric acid solution.

PABU efficiently inhibits the corrosion of mild steel in 5% HCl solutions (devaraj karthik et al., 2011). The corrosion rate decreased considerably with an increase in concentration of inhibitor. These experimental values prove that as the efficiency of inhibition increases with concentration of inhibitor increases. The temperature increases the rate and influences adsorption equilibrium and kinetics as well. The effect of temperature on the corrosion inhibition with and without inhibitor are shown. It can be seen that the weight loss increases with temperature in the absence and presence of inhibitor. Adsorption and desorption of inhibitor molecules continuously occur at the metal surface and an equilibrium exists between two processes at a particular temperature. With increase of temperature, the equilibrium between adsorption and desorption processes is shifted to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant. It explains the lower inhibition efficiency at higher temperature. PABU is able to maintain it's inhibition at about 80.85% at 303K and the inhibition efficiency is slightly decreased to 63.79% at 353K. The corrosion inhibition property of these compounds is attributed to their molecular structure. The planarity and the lone pair electrons in the hetero atoms are important features that determine the adsorption of these molecules on the metallic surface. The effect of inhibitors adsorbed on metallic surfaces in acid solutions, is slow down the cathodic and anodic process of dissolution of the metal. This is due to the formation of a barrier of diffusion or by means of the blockage of the reaction sites and there by reducing the corrosion rate.

CONCLUSION

The synthesized new Mannich base 1-((4-chlorophenyl)(pyridine-4-ylamino)methyl)urea have been characterized on the basis of above spectroscopic method and synthesized compound assigned for corrosion inhibition evaluation and discussion.

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