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ANTICORROSION ACTIVITY OF 1,3-BIS-[PHENYL-(PYRIDIN-2-YL AMINO)-METHYL]-UREA (PABU) FOR MILD STEEL IN HYDROCHLORIC ACID MEDIUM

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#### ABSTRACT

The Mannich base 1,3-bis-[phenyl-(pyridin-2-yl amino)-methyl]-urea (PABU) was prepared and characterized by IR spectroscopic method. The anticorrosion activity of this ligand has been investigated by weight loss and electrochemical method. The inhibition efficiency values determined by the above methods were in good agreement. The ligand has the better performance in HCl medium. The experimental results revealed that inhibition efficiency increases with ligand concentration but decreases with acid concentration and temperature. The electrochemical impedance spectroscopy result shows that the ligand is mixed type inhibitor. The Scanning Electron Microscope (SEM) image and IR spectra confirms the chemisorption phenomenon of PABU on mild steel in HCl medium.

Keywords: Mild steel; SEM; FT-IR spectra; EI spectroscopy; Weight loss method.

## 1. INTRODUCTION

Corrosion inhibition of mild steel is a matter of theoretical as well as practical importance [1]. Acids are widely used in industries such as pickling, cleaning, descaling etc., Because of their aggressiveness; inhibitors are used to reduce the rate of dissolution of toxic metals into the environment [2-7]. Organic compounds containing sulphur, phosphorus, nitrogen and oxygen atoms and  $\pi$ -electrons in triple or conjugated double bonds are usually good corrosion inhibitors [8].

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 thereby reducing the corrosion rate [9].

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 [10, 11]. The synthetic utility of Mannich reaction is evident from its application in the synthesis of many natural products and biologically important compounds [12-14], such as anti-tubercular, antimalarial, vasorelaxing, anti-cancer, and analgesic drugs [15].

The objective of this study is to investigate the corrosion behavior of PABU on mild steel in 1 M HCl solution at 303-353 K using weight loss method and electrochemical impedance techniques. The effects of temperature, acid concentration, immersion time were also studied.

#### 2. EXPERIMENTAL

#### 2.1. Preparation of the inhibitor

1,3-bis-[phenyl-(pyridin-2-ylamino)-methyl]-urea was synthesized by Mannich condensation reaction between urea, benzaldehyde and 2-amino pyridine in 1:1:1 mol ratio. Urea (6.0g, 0.1M), benzaldehyde (10mL, 0.1M) and 2-amino pyridine (9g, 0.1M) were taken in equimolar ratio. A concentrated aqueous solution of urea was prepared. Benzaldehyde was added in drops with urea at constant stirring of the solution. To the above mixture aqueous solution of 2-amino pyridine was added drop by drop. The synthetic route was shown in scheme 1 and the mixture first became oily and then slowly turned into a yellow crystalline mass which was separated by suction filtration and washed several times with water and acetone. The product was dried at 60°C and recrystallized using methanol by slow evaporation method [16]. PABU is a pale yellow solid and its melting temperature is 106°C. Molecular formula is  $C_{27}H_{31}N_6O$ and Molecular weight is 455.57. It is insoluble in water,

but partially soluble in chloroform, carbon tetrachloride, acetone, toluene, dimethyl formamide, ether, and benzene and completely soluble in methanol, propanol and butanol. The concentration of inhibitor for weight loss method and electrochemical studies ranges from 150ppm - 450ppm.



Scheme 1: Synthesis of PABU ligand



Fig.1: Structure of 1,3-bis-[phenyl-(pyridin-2-ylamino)-methyl]-urea PABU

#### 2.2. Materials used for the Corrosion Studies

Weight loss and electrochemical method were studied using mild steel plates having composition (wt %): 98.84% Fe, 0.40% P, 0.39% Mn, 0.18% Si, 0.13% C, 0.04% S and 0.025% Cu. The mild steel plates having dimension 5cm× 2.4cm× 0.2cm were abraded using 1/0, 2/0, 3/0, and 4/0 grade of emery papers respectively, washed in absolute ethanol and then in acetone, dried and stored in moisture free desiccator before use [17]. 1M HCl acid solution was prepared by dilution of analytical grade 37% HCl with triple distilled water. The acid concentration is varied from 10%-30% for weight loss method and electrochemical method.

#### 2.3. Weight loss measurement

The mild steel plates were weighed before immersion and suspended in the beaker with the help of rod and hook [18]. The plates were taken out, rinsed several times in deionized water, cleaned, dried using acetone, and re-weighed. The weight loss, in grams, was taken as the difference in the weight of the mild steel plates before and after immersion in different test solutions. Then the tests were repeated at different temperatures and time. For the sake of convenience, experiments were carried out in duplicate. Inhibition Efficiency has been determined by the following relationship (1)

Inhibition Efficiency (%) =  $[(W_b - W_i)/W_b] \times 100....(1)$ 

Where,  $W_b$  and  $W_i$  are the weight loss without inhibitor and with inhibitor, respectively [19].

The corrosion rate has been determined by the following relationship

Corrosion rate  $(mm/y) = (87.6 \times W) / (A \times T \times D)$ 

Where, W=weight loss in g; A=area in  $cm^2$ ; T=time of immersion in hours and D=density in g/cm<sup>3</sup> [19].

## 2.4. Effect of Temperature and Acid concentration

The temperature was varied from 303-353 K for weight loss method. The effect of inhibition efficiency at various temperature and acid concentration was studied. The time interval for corrosion studies was maintained at 60 mins. The acid concentration was varied from 10-30%. Each experiment was carried out second time to get good reproducibility. Weight loss measurements were performed with and without the inhibitor. Percentage of inhibition efficiency at various temperatures and acid concentration were calculated.

#### 2.5. Electrochemical measurements

A conventional three electrodes setup was used for EIS measurements. Mild steel plate was used as working electrode with an exposing area of 1 cm<sup>2</sup> to the electrolyte, Ag/AgCl(s)/KCl (saturated) as reference electrode and platinum wire as auxiliary electrode. The EIS measurements were studied over frequency ranges from 0.01Hz-10 KHz at open circuit potential with signal amplitude of 0.01V. In EIS spectroscopy, we can calculate  $C_{dl}$  using the formula:

The inhibition efficiency was calculated from the impedance measurements, using the equation [20]:

Inhibition efficiency (%) =  $[(R_{et} (inh) - R_{et} (blank))/R_{et} (inh)] X100$ 

Where,  $R_{ct}$  (inh) is the charge transfer resistance in the presence of inhibitor and  $R_{ct}$  (blank) is the charge transfer resistance in the absence of inhibitor.

The capacitance of double layer was calculated from Nyquist plot by using the following Equation [20]

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}}$$

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Where,  $f_{max}$  is the frequency at which the imaginary Component of the impedance  $(Z_{max})$  is maximal.  $R_{ct}$  resistance for charge transfer.

These two have been obtained by the difference between lower and higher values in X-axis and Y-axis respectively.

## 2.6. FT-IR spectra

FT-IR spectra for PABU and the dried product formed between finely powdered mild steel and PABU were recorded between a frequency range of 4000cm<sup>-1</sup> to 400cm<sup>-1</sup> in KBr medium [21, 22].

## 2.7. SEM analysis

The surface morphology of the exposed surface of mild steel plates in presence of inhibitor and absence of inhibitor was studied using Scanning Electron Microscope (SEM model: HITACHI S-3000 H) [23-25].

#### 3. RESULTS AND DISCUSSION

# 3.1. Weight loss, corrosion rate and Inhibition Efficiency

Table 1 shows that Inhibition Efficiency was increased with increase in PABU concentration. For this 15% acid solution was used at 303 K and for 60 mins. Hence weight loss and corrosion rate tends to decrease as PABU concentration increases. It is clear from the Table-1 inhibition efficiency is inversely proportional to weight loss and corrosion rate. Fig.2 shows the increase in inhibition efficiency with raise in PABU concentration. The higher inhibition efficiency of PABU is due to nitrogen atoms, oxygen atoms and aromatic rings present in it. The lone pair of electrons in hetero atoms will coordinate with liberating Fe ions from mild steel so that the electron production reduces hence weight loss decreases.

## Table.1 Variation of IE with increasing PABU concentration at 303 K

<b>Concentration of HCl</b>	<b>Concentration of PABU</b>	Weight loss	<b>Corrosion Rate</b>	Inhibition
(%)	(ppm)	(g)	(mmpy)	Efficiency (%)
	Blank	0.0343	0.0312	=
	150	0.0227	0.0207	33.65
10	250	0.0127	0.0116	62.82
	350	0.0267	0.0243	22.11
	450	0.0247	0.0225	27.88
	Blank	0.0461	0.0419	-
	150	0.0221	0.0201	52.02
15	250	0.0281	0.0256	38.90
	350	0.0154	0.0140	66.58
	450	0.0165	0.0150	64.20
	Blank	0.0582	0.1059	-
	150	0.0559	0.1017	3.9
20	250	0.0519	0.0944	10.8
	350	0.0450	0.0819	22.66
	450	0.0351	0.0638	39.75
	Blank	0.0485	0.0442	-
25	150	0.0391	0.0356	19.45
	250	0.0385	0.0350	20.81
	350	0.0377	0.0343	22.39
	450	0.0377	0.0343	22.39
	Blank	0.0603	0.0549	-
	150	0.0578	0.0526	4.18
30	250	0.0551	0.0501	8.74
	350	0.0481	0.0437	20.40
	450	0.0401	0.0365	33.31



Fig.2: Variation of IE with increasing PABU concentration at 303 K

## 3.2. Effect of Temperature and Acid concentration

Table 2 shows that inhibition efficiency decreases as the temperature and acid concentration increases. Because the adsorption tendency of PABU was only to a certain limit. After that, it started desorption from the mild steel. This may overcome by increasing the PABU concentration at higher extent so that adsorption will again take place. This is due to weakening of adsorbed inhibitor film on the mild steel plate. Otherwise equilibrium will shift towards right which denotes desorption will be high hence there was a decrease in inhibition efficiency. It was found from Table 2 that inhibition efficiency decreases with increase in acid concentration; this is due to increase in aggressiveness of the acid.

<b>Concentration of HCl</b>	<b>Concentration of PABU</b>	Weight loss	<b>Corrosion Rate</b>	Inhibition
(%)	(ppm)	(g)	(mmpy)	Efficiency (%)
	Blank	0.0940	0.0855	-
	150	0.0465	0.0423	50.52
10	250	0.0480	0.0437	48.88
	350	0.0572	0.0521	39.06
	450	0.0410	0.0373	56.37
	Blank	0.3500	0.3250	-
	150	0.3058	0.2840	12.62
15	250	0.2749	0.2553	21.45
	350	0.2170	0.2015	38.00
	450	0.2018	0.1874	42.33
	Blank	0.6591	0.6246	-
	150	0.6337	0.6005	3.85
20	250	0.5353	0.5073	18.78
	350	0.4864	0.4609	26.21
	450	0.3373	0.3196	48.83
	Blank	2.4018	2.3235	-
	150	1.0288	0.9952	57.16
25	250	0.9206	0.8906	61.67
	350	1.2327	1.1925	48.67
	450	0.1999	0.1933	91.68
	Blank	1.3088	1.2931	-
	150	1.2588	1.2437	3.82
30	250	1.0408	1.0283	2.047
	350	0.9059	0.8950	30.78
	450	0.8824	0.8718	32.58

Table.2 Variation of IE with increase in PABU concentration at 333 K





Fig.3: Variation of IE with increase in PABU concentration at 333 K

Fig.4: Variation of IE with increase in PABU concentration at 353 K

Table.3 Variation of IE with increase in PABU concentration at 35	3 K
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<b>Concentration of HCl</b>	<b>Concentration of PABU</b>	Weight loss	<b>Corrosion Rate</b>	Inhibition
(%)	(ppm)	(g)	(mmpy)	Efficiency (%)
	Blank	1.0875	0.9902	-
	150	0.7339	0.6682	32.52
10	250	0.6540	0.5954	39.87
	350	0.5521	0.5027	49.23
	450	0.4972	0.4527	54.28
	Blank	0.5077	0.4715	-
	150	0.4416	0.4101	13.02
15	250	0.3829	0.3556	24.58
	350	0.3245	0.3014	36.07
	450	0.3204	0.2975	36.90
	Blank	2.4631	2.3343	-
	150	1.2999	1.2319	47.22
20	250	1.0636	1.0080	56.82
	350	0.8453	0.8011	65.68
	450	0.8141	0.7715	66.94
	Blank	2.6577	2.5711	-
	150	2.0520	1.9827	22.88
25	250	1.7473	1.6904	34.25
	350	1.5496	1.4991	41.69
	450	1.3324	1.2889	49.86
	Blank	4.0055	3.9576	-
	150	3.2280	3.1894	19.41
30	250	3.3370	3.2971	16.68
	350	2.6098	2.5785	34.84
	450	2.4271	2.3950	47.30

## 3.3. Electrochemical Impedance Measurements

The values of  $R_{ct}$ ,  $C_{dl}$  and IE which were derived from Nyquist plots as shown in Fig. 5. It can be seen from Table-4 resistance per charge transfer tends to increase, because with higher concentration of PABU the

liberation of electrons from mild steel plates decreased so that resistance increased. Also capacitances for double layer decreased because of adsorption, the thickness of double layer become increased. This shows the increase in surface coverage area with increasing PABU concentration.

Conc. of	f	<b>R</b> <sub>ct</sub>	C <sub>dl</sub>	I.E
PABU(ppm)	1 <sub>max</sub>	$(\Omega cm^2)$	(µF/cm²)	(%)
Blank	30	82.5	0.000064	-
150	38	109	0.000038	40.62
250	46	118	0.000029	54.68
350	48	122	0.000027	57.81
450	52	136	0.000022	65.62

#### Table.4 Values of IE from EI spectroscopy

Table.5 Values of IE from weight loss method

Conc. of PABU (ppm)	Weight Loss (g)	Corrosion Rate (mmpy)	I.E (%)
Blank	30	82.5	0.000064
150	38	109	0.000038
250	46	118	0.000029
350	48	122	0.000027
450	52	136	0.000022



Fig.5: Nyquist plot of PABU in 15% hydrochloric acid 4. SEM



(a)



# Fig. 6: SEM photograph of the mild steel plates in presence and absence of inhibitor (PABU).

The inhibited metal surface is smoother than the uninhibited surface indicates that a thin layer of inhibitor adsorbed on metal surface to protect the mild steel from corrosion against HCl attack.

#### 5. FT-IR SPECTROSCOPY

The Fig.7 shows that the IR spectrum of PABU and the adsorbed product on the surface of mild steel in presence of inhibitor.



Fig.7: FT-IR Spectra (a) for PABU (b) for adsorbed product on the mild steel surface

On comparing Figure (a) and (b) clearly shows that the certain peaks had been disappeared completely and some have shifted to higher frequency region, providing that some interaction/ adsorption has been taking place over the metal surface. The -NH stretching shifted from 3250 to 3490 cm<sup>-1</sup> and CO stretching shifted from 1627 to 1750 may suggest that there is an interaction between PABU and the metal surface.

## 6. CONCLUSION

The weight loss study clearly depicts that corrosion inhibition efficiency of mild steel plates increases with increase in inhibitor concentration and decreases as the temperature, time and acid concentration are raised. The enhanced adsorption on the metal surface by inhibitor with increase in concentration is illustrated from the Nyquist plot. The adsorption of the inhibitor on the metal surface is accredited to the lone pair of electrons present in the hetero atoms of the PABU. This is further confirmed FT-IR from spectral studies. The electrochemical parameters specify the mixed mode of inhibition. The photographs of the SEM study evidently focus the protective nature of the extract over mild steel. A maximum inhibition efficiency of 92% was obtained for PABU. Therefore, it is obvious that the PABU is an effective, eco-friendly and alternate corrosion inhibitor for mild steel in HCl medium.

#### 7. REFERENCES

- Ali SA, Saeed MT, Rahman SV. Corrosion Sci., 2003; 45(2):253-266.
- Lagrenee M, Mernari B, Bouanis M, Traisnel M, Bentiss F. Corrosion Sci., 2002; 44(3):573-588.
- Quraishi MA, Sardar R. Corrosion Sci., 2002; 58(9):748-755.
- Singh AK, Quraishi MA. Corrosion Sci., 2010; 52(4):1373-1385.
- Quraishi MA, Ansari FA, J. Appl. Electrochem., 2003; 33(3):233-238.
- Singh AK, Quraishi MA, J. Appl. Electrochem., 2010; 40(7):1293-1306.
- Quraishi M.A., Ahamad I., Singh A. K., Shukla S. K., Lal B., Singh V., Chem. Phys., 2008; 112(3):1035-1039

- Jamal Abdul Nasser A., Anwar Sathiq M. International Journal of Engineering Science and Technology, 2010; 2(11):6417-6426.
- 9. Negm NA, Zaki MF, Salem MA, J. Surfact. Deterg., 2009; **12:**321-329.
- Rajeswari S, Venkatesa Prabhu G, Tamilvendan D, Ramkumar V. J. Chem. Crystallogr., 2009; 39:650-654.
- 11. Mannich bases chemistry and uses by Maurilio Tramontini, Luigi Angiolini.
- 12. Heaney H, Trost Fleming BM. In Comprehensive Organic Synthesis, 1991; 2:953-973.
- 13. Overman LE, Ricca DJC, Fleming BM. In Comprehensive Organic Synthesis, 1991; 2:1007-1046.
- Arend M, Westerman BA. Chem. Int. Ed. Engl, 1998; 37:1044.
- 15. Franklin S, Tamilvendan D, Venkatesa Prabhu G, Balasubramanian T. J Chem Crystallogr, 2011; 41.
- 16. Manjula J. Thesis Bharathidasan University
- 17. Eno E, Ebenso Ime B, Obot. Int. J. Electrochem. Sci., 2010; 5: 2012-2035.
- Fontana MG. Corrosion Engineering, third ed., McGraw- Hill, Singapore, 1986.
- Parameswari K. Electrochem. Acta., 2010; 28:189-201.
- Vinod Kumar KP, Sankara Narayanan Pillai M, Rexin Thusnavis G. J. Mater. Environ. Sci., 2010; 1(2):119-128.
- 21. Sethuraman MMG, Bothi Raja P. Pigm Res. Technol., 2005; 34:327.
- 22. Muhamath, Basha Mubarak Ali, Kulanthai Kannan, J. Appl. Sci. Environ. Manage., 2009; 13(1):27-36.
- 23. Odiongenyi AO, Odoemelam SA, Eddy NO. *Portugaliae Electrochimica Acta.*, 2009; **27(1)**:33-45.
- Anwar Sathiq M, Jamal Abdul Nasser A, Mohamed Sirajudeen P. *E-Journal of Chemistry.*, 2011; 8(2):621-628.
- 25. Sheela G, Muralidharan VS, Malathy P. Indian J. chem. Tech., 2005; **12:**466-471.