Inhibition of Mild Steel Corrosion in 1M H$_2$SO$_4$ Medium by BenzimidazoleMannich bases

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ABSTRACT

The corrosion inhibition behaviour of two synthesized Mannich bases has been investigated for mild steel in 1M H$_2$SO$_4$ by weight loss and electrochemical techniques.The inhibition efficiency depends on concentration of the inhibitor and temperature. The inhibitors function by adsorption on mild steel surface and obey Langmuir isotherm indicating monolayer adsorption on the surface. Thermodynamic parameters show that the adsorption of the inhibitors occurs through electrostatic interaction. Polarization studies reveal that the inhibitors behave as mixed type in 1M H$_2$SO$_4$ affecting both anodic metal dissolution and cathodic hydrogen evolution. SEM studies show the formation of surface adsorptive film of the Mannich bases on the mild steel surface.

Key words: Inhibitors, Mannich bases, Potentiodynamic polarization, Langmuir adsorption isotherm, Electrochemical impedance.

INTRODUCTION

Mild steel is largely used in industries as structural material, which undergoes corrosion easily in acidic medium. Acids are widely used for various industrial processes such as pickling, cleaning, descaling, acidizing etc. Because of the aggressiveness of the acids, inhibitors are used to reduce the rate of dissolution of mild steel. Compounds containing nitrogen, sulphur and oxygen have been reported as excellent inhibitors[1,2]. Nitrogen and sulphur atoms in the molecules are the active centers for the process of adsorption of the compounds on the metal surface to form a protective layer[3].Mannich bases are pharmaceutically important compounds and reported to show a wide range of bioactivities. They are also used in polymer chemistry especially as paints and surface active agents. Though Mannich bases are known for many decades, it was only recently that they have been used as corrosion inhibitors.The versatile utility of Mannich bases and

their complexation characteristics with many transition metal ions prompted us to prepared two new Mannich bases and evaluate their corrosion inhibition performance for mild steel in 1M H_2SO_4. The investigation is carried out using electrochemical and gravimetric measurements(4)
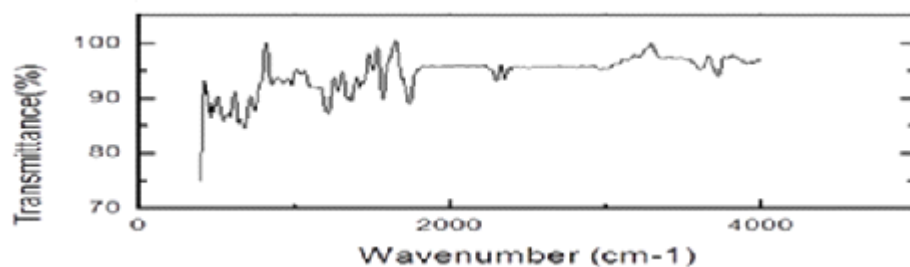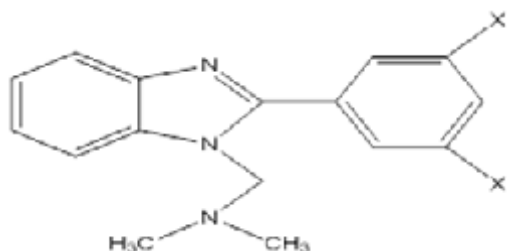
Methodology
Chemical composition of the mild steel

The experiments were performed with cold rolled mild steel specimen of chemical composition (C=0.20%,Mn=1%,Si-0.05%,S=0.025%,P=0.25% and Fe=98%).

Structure of the Mannich bases

5-(1-((dimethylamino/dimethylnitro) methyl)-1H-benzo[d]imidazol-2-yl)benzene-1,3-diamineThe structure was confirmed by FTIR Spectra. (KBr) υ cm^{-1}: 1215.21(C-N str.), 1572.05 (C=C str.), 1678.11 (C=N), 1281.75 (C-H bend.), 3603.18 (NH$_2$)
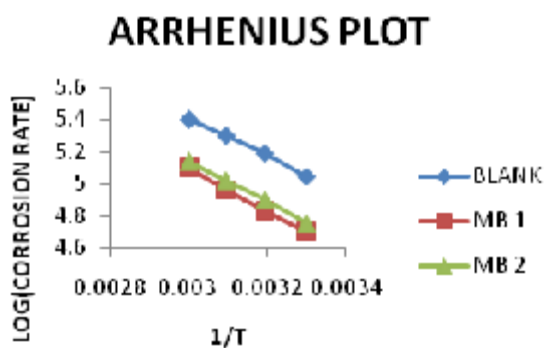

Fig. 1: FTIR Spectrum of MB1
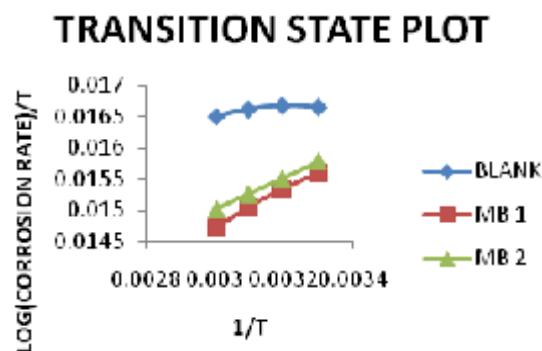

Fig. 2: Arrhenius plot for MB 1&MB 2

Fig. 3: Transition State plot for MB 1& MB2
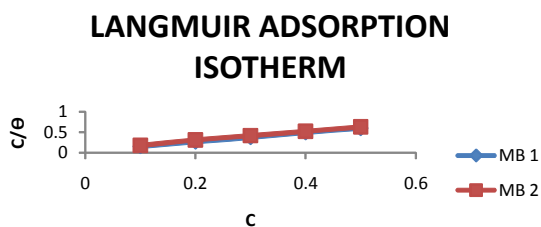
**Fig. 4: Langmuir Adsorption Isotherm
for the inhibitors MB 1 & MB 2**

Corrosion monitoring methods

Weight loss measurements were carried out with rectangular mild steel plates of dimension 3cm× 1cm× 0.1cm. The polished, preweighed plates were immersed in 1M H_2SO_4 containing different concentrations of the inhibitors for 3 hrs and then reweighed. From the loss in mass, inhibition efficiency was calculated.
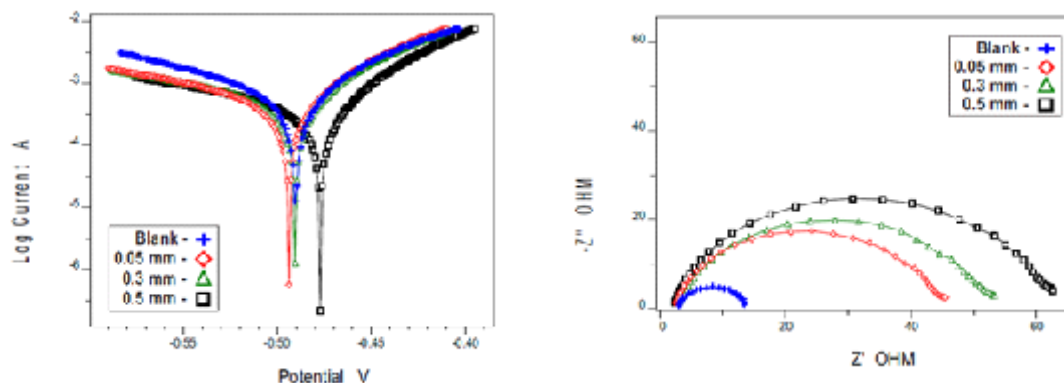
Fig. 5: Polarisation (Tafel) plot and Nyquist plot for mild steel in 1M H$_2$SO$_4$ containing various concentrations of the inhibitor MB 1
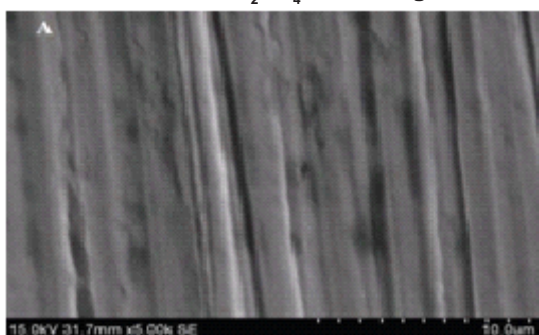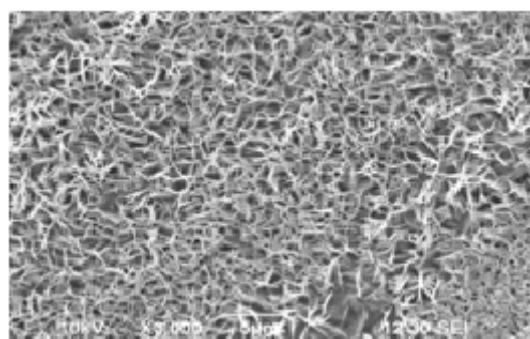
Fig. 6: Polishedmildsteel
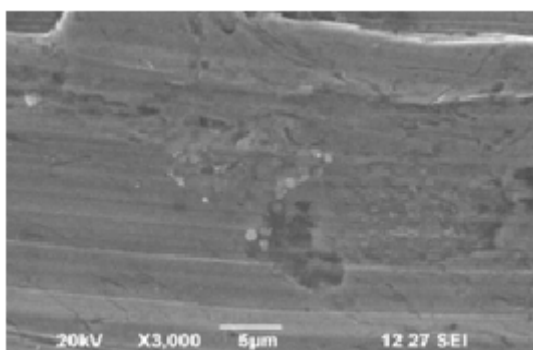
Fig. 7: Immersed in1M H$_2$SO$_4$

Fig. 8: Immersed in1M H$_2$SO$_4$

The electrochemical studies were performedon IVIUM Compactstat(potentiostat/galvanostat), using mild steel rod with exposed area 0.785 cm^2. The potential range is -200 to +200 mV with respect to the open circuit potential at a scan rate of 1mV/sec. For impedance measurements, the sweep frequency is from 10Hz to 0.01Hz with a signal amplitude of 10mV.SEM micrographs of the

mild steel immersed in 1M H$_2$SO$_4$ with and without inhibitor and the morphology was compared.

RESULTS AND DISCUSSIONS

Weight loss measurements

The value of percentage inhibition efficiency (IE%) obtained from weight loss method at different concentrations of the inhibitors in 1 M H$_2$SO$_4$ at room temperature are summarized in Table (**1**). The values show thatboth the inhibitors MB 1& MB 2 inhibit the corrosion of mild steel in H$_2$SO$_4$ solution,at all concentrations used. Maximum inhibition efficiency was shown at 0.5mM concentrationof the inhibitor.The behavior may be attributed to an increase in surface coverage, θ by the adsorption of inhibitors on the mild steel surface, in the aggressive solution, which restricts the dissolution of the metal.

Influence of Temperature

　　　Inorder to study the effect of temperature on corrosion inhibition of mild steel in acid and to determine the activation energy for the corrosion process, the weight loss studies were carried out at higher temperatures(303-333K). Analysis of the resultsin Table-2 show that the inhibition efficiency decreased with increase intemperature. This may

be attributed tothe desorption of the inhibitor molecule from metal surface at higher temperatureindicating that the inhibitors get adsorbed predominantly by physisorption on the mild steel surface (5).

Thermodynamic parameters

　　　Thermodynamic parameters such as Ea, ΔG, ΔH and ΔS were calculated using Arrhenius plot (Fig.2) and Transition state plot(Fig.3). Ea value is greater in the presence of inhibitor than that in blank acid. The increase in Ea in the presence of inhibitor is typical of physisorption[6]. Negative ΔG^0_{ads} values indicate spontaneity of the adsorption processand the values upto 40kJ/molsuggests electrostatic interactions between the charged molecules of the inhibitor and the charged metal surface (i.e.,physisorption)[7]. The negative value of ΔH^0 reflects the exothermic nature of dissolution process. The value of entropy change ΔS^0 in the presence of inhibitor is negative, which implies that

Table 1: Inhibition efficiencies of the inhibitors at various concentrations for mild steel corrosion in 1M H_2SO_4 at 30±1⁰ C

Concentration, mM	Inhibition Efficiency,%	
	MB 1	MB 2
0.1	57.55	56.38
0.2	65.55	64.03
0.3	79.68	71.92
0.4	80.58	80.15
0.5	83.61	82.40

Table 2: Inhibition efficiency at 0.5mM concentration of the inhibitors for mild steel corrosion in 1M H_2SO_4 at various temperatures

Name of the compound	Temperature, K	Weight loss,g	Inhibition efficiency,(%)	Corrosion rate,mpy
Blank	303	0.0609	-	76627.43
	313	0.1152	-	144950.4
	323	0.1443	-	181565.5
	333	0.2486	-	312801
MB 1	303	0.0422	83.61	53,101.64
	313	0.0518	79.88	65,181.64
	323	0.0575	77.66	72,354.14
	333	0.0622	75.84	78,268.30
MB 2	303	0.0453	82.40	57,002.48
	313	0.0566	78.01	71,221.64
	323	0.0673	73.86	84,685.80
	333	0.0743	71.14	93,494.13

Table 3: Thermodynamic Parameters for mild steel corrosion in 1M H_2SO_4

Name of the inhibitor in mM	Activation energy, E_a (kJ/mole)	$-\Delta G^0_{ads}$(kJ/mole)				$-\Delta H^0$ kJ/mole	$-\Delta S^0$ kJ/mole
		303 K	313 K	323K	333 K		
Blank	22.695	-	-	-	-	-	-
MB 1	25.666	14.67	14.61	14.81	15.05	62.43	0.9988
MB 2	24.595	14.49	14.39	14.39	14.56	58.87	0.9966

**Table 4: Corrosion parameters for mild steel with selected concentration
of the inhibitors in 1M H$_2$SO$_4$ bypotentiodynamic polarization method**

Name of the compound	Concentration mM	Tafel slope, mV/decade		-E$_{corr}$, mV	I$_{corr}$ (µF/cm²)	Inhibition Efficiency(%)
		ba	bc			
Blank		69	113	492.1	287.7	
MB 1	0.05	61	143	495	55.43	80.74
	0.3	62	155	491.8	53.95	81.26
	0.5	55	154	478.1	42.05	85.40
MB 2	0.05	59	146	493.2	44.79	84.46
	0.3	56	156	486.8	37.33	87.03
	0.5	51	146	478.1	27.22	90.54

**Table 5: Impedance parameters for corrosion of mild steel at
the selected concentrations of the inhibitor in 1M H$_2$SO$_4$**

Name of the compound	Concentration(mM)	R$_{ct}$ (ohm/ cm²)	C$_{dl (µF)/cm}^2$	Inhibition Efficiency(%)
Blank		15.08	28.2	
MB 1	0.05	35.29	29.2	57.26
	0.3	40.14	28.6	62.43
	0.5	51.31	26.3	70.61
MB 2	0.05	34.65	33	56.47
	0.3	47.74	32.3	68.41
	0.5	64.36	30.8	76.56

the activated complex represents an association rather than dissociation.

Langmuir Adsorption Isotherm

Basic information on the interaction between the surface of mild steel and inhibitor can be determined by studying adsorptionisotherms. The commonly used adsorption isotherms are the Langmuir, Temkin, Frumkin, and Flory–Huggins. Thedegree of surface coverage(θ) for different concentrations of the inhibitors have been evaluated. The data were testedgraphically to determine a suitable isotherm. A straight line with correlation coefficient (R²) almostequal to 1.0, was obtained on plotting C$_{inh}$/, versus C$_{inh}$ is shown in Fig. 4, indicatingthat adsorption of the inhibitors on the mild steel surface obeys the Langmuir adsorption isotherm. It is an ideal isotherm for physical or chemical adsorption where there is no interaction between the adsorbed molecules(8). According to Langmuiradsorption isotherm, the

surface coverage (θ) is related to inhibitor concentration (Cinh) by equation (1) (9):

$$C/\theta = 1/K + C \qquad ...(1)$$

Where 'K' is the equilibrium constant of adsorption.The slopes of straight lines (Fig.4) were found to be very close to unity. This means that, adsorbed molecule occupies onlyone site and it does not interact with other adsorbed species (10) Potentiodynamic polarization curves for the corrosion of mild steel in 1M H$_2$SO$_4$ in the absence and presence of different concentrations of MB 1 at room temperature is shown in Fig.5.Thecorrosion current density (I$_{corr}$), Tafel slopes [anodic (ba) and cathodic (bc)] were calculated by extrapolation of linear parts of anodic and cathodic curves to the corresponding corrosion potential (E$_{corr}$). The percentage inhibition efficiency (IE %) and the degree of surface coverage (θ) were calculated.

The electrochemical parameters, determined from Tafel polarization curves are summarized in Table 4. The datashowed that the current density decreased in the presence of inhibitors than in its absence. The(%) inhibition efficiencyincreased with increasing inhibitor concentrations. This indicates that the inhibitor molecules are adsorbed on the metalsurface. The inhibition was more pronounced with increasing inhibitor concentration.Tafel lines are shifted to both negative and positive potentials with respect to the blank curve by increasing the concentration of the inhibitor,also there only slight changes in E_{corr} value.The I_{corr} value decreases when the concentration of the inhibitor increases.This behavior indicates that both anodic metal dissolution and cathodic hydrogen evolution mechanism are affected in the presence of the inhibitorand inhibitors act as mixed-type.

Electrochemical Impedance Spectroscopy

Nyquist plots of mild steel in 1 M H_2SO_4 solution in the absence and presence of different concentrations of the inhibitor MB 1 is shown in Fig. 7.The charge transfer resistance (R_{ct}) values were calculated from the difference in the Z^1 atlow and high frequencies. The inhibition efficiency, (IE %) and the degree of surface coverage (₃) of the Mannich bases can be calculated from the charge-transfer resistance according to Eq. (3) (11):

$$IE = R_{ct}-R_{ct}*/R_{ct} \times 100 \qquad ...(3)$$

Where,$R_{ct}*$ = The charge-transfer resistances for uninhibited solution.

R_{ct}= The charge-transfer resistances for inhibited solution.

C_{dl}, double layer capacitance obtained from the Nyquist plots and the calculated inhibition efficiency values (IE_{EIS} %) arereported in Table 5. It is apparent from the table that the value of R_{ct}increased with increasing concentration of the inhibitors. The increase in R_{ct}values is attributed to the formation of an insulating protective film at the metal/solution interface. The value of C_{dl} decreased upon the addition of the inhibitor, suggesting, a decrease in the localdielectric constant and/or an increase in the thickness of the electrical double layer, indicate that the Mannich basesfunction by the formation of a protective layer at the metal surface[12]. The size of the semicircle increases with inhibitor concentration, indicating that the charge transfer process as the controlling factor of the corrosion of mild steel[13].

Scanning Electron Microscopy Studies

The surface morphology of mild steel surface was evaluated by scanning electron microscopy (SEM). Figures 8, 9 & 10 show the scanning electron micrographs of the polished mild steel surface and mild steel immersed in sulphuric acid medium without and with inhibitor MB 1. It is clear that in the absence of the inhibitor, the surface is highly corroded. However in the presence of inhibitor the rate of corrosion is suppressed and the inhibitor forms a protective layer on the surface that prevents the attack of acid on the metal[14].

Corrosion inhibition mechanism

The results obtained from all the studies show that both the Mannich bases have almost same inhibition efficiency, which may be explained as follows. The Mannich bases have almost similar structure except for the substituents on the phenyl ring. The Mannich bases are adsorbed on the mild steel surface through the nitrogen atoms of the benzimidazole ring in a flat orientation. The benzimidazolyl group attached with the t-amino group (dimethylaminomethyl) group gives large steric effect to the disubstituted phenyl ring at position-2 pushing it to a perpendicular plane. Hence the substituents on the phenyl ring have little influence on the inhibition performance.

CONCLUSION

The synthesized Mannich bases were found to be very good inhibitors for the corrosion of mild steel in 1M H_2SO_4 and the efficiency increases with increase in concentration of the inhibitor and decreases with temperature. The inhibitors act by adsorption and obey Langmuir Isotherm. Electrochemical studies show that the inhibitors are mixed type.

REFERENCES

1. Lagrenee, M.;Mernari, B.; Bouanis, M.; Traisnel, M.; Bentiss, F. *Corro. Sci.*,**2002,**44, 573-588

2. Quraishi, M. A.;Sardar,R. *Corro.***, 2002**, 58,748-755

3. Upadhyay, R. K.; Mahur,S. P. *E-J. Chem.*,**2007,** 4, 408-414.

4. Verma, C. B.; Quraishi, M. A.; Ebenso, E. E. *Int.J.ofElectrochem. Sci.*, **2013**,8, 10851-10863

5. Praveen, B. M.; Venkatesha, T. V. *Int. J. Electrochem. Sci.*,4,**2009**, 267-275

6. Dehri, I.;Ozcan, M. *Mater. Chem. Phy.,***2006,** 98, 316-323.

7. Popova, S.; Sokolova, A., Raicheva, S.; Christov, M. *Corro. Sci.,***2003**, 45, 33-58

8. Bouklah, M.;Benchat, N.; Hammouti, B.;Aouniti, A.;Kertit, S. *Mater. Lett.,***2007**,60,1901-1905**.**

9. Jayaprabha, C.; Sathiyanarayanan, S.;Venkatachari, G. *Mater.chem.&phy.*,**2005**, 107,350-355.

10. Li,X. H.; Deng, S. D.; Mu,G. N.; Fu, H.;Yang, F. Z. *Corros. Sci.,***2008**, 50, 420-430

11. Hamed, E. *Mater.Chem. Phys.,***2010**,121, 70-76.

12. El-Haddad,M. N. *Int. J. Biolog.Macromol.*,**2013,**55, 142-149.

13. Bosch, R.W.; Hubrecht, J.; Bogaerts, W. F.; Syrett,B. C. *Corro.,***2003**, 57, 60-70.

14. HazwanHussin, M.;Jain Kassim,M. *Int. J. Electrochem. Sci.***,** 6,**2013**,1396-1414