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Efficiency of Some Newly Synthesized Mannich Bases as Corrosion Inhibitor for Mild Steel in HNO_3 solution

P. Sharma, R. K. Upadhyay[*] and A. Chaturvedi

Synthetic and Surface Science Laboratory, Department of Chemistry, Govt. College Ajmer, Rajasthan, INDIA

Email ID: alwayz_rajesh@yahoo.co.in

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ABSTRACT: Weight loss and thermometric methods have been used to study the corrosion inhibition of mild steel in HNO_3 solution by four newly synthesized Mannich bases viz 3-oxo-3-phenyl-N,N-dimethyl propanamine hydrochloride (MB_1), 3,5-dioxo-5-phenyl-N,N-dimethyl pentanamine hydrochloride(MB_2), 2,2-dimethyl-3-oxo-N, N dimethyl butanamine hydrochloride (MB_3) and 3-oxo-N,N-dimethyl butanamine hydrochloride((MB_4).Efficiency of inhibitor increases with increasing concentration of inhibitor whereas it decreases with increasing concentration of acid. Results of inhibition efficiencies obtained from both methods are in good agreement with each other.

Keywords: Efficiency, surface coverage, Reaction Number, Weight loss, Mannich base.

INTRODUCTION

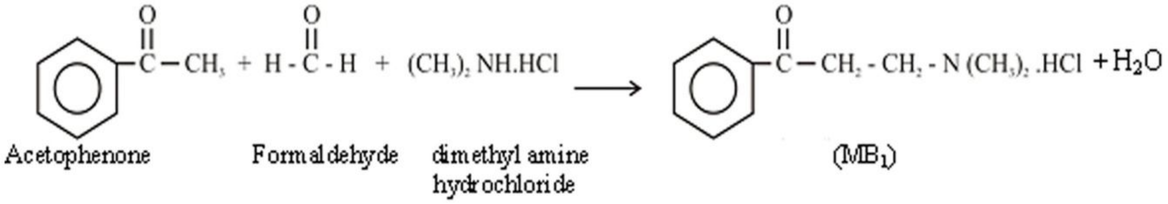
Mild steel finds a variety of applications industrially, in mechanical and structural purposes like bridge work, buildings, boiler plates, steam engine parts and automobiles. Mild steel is prone to atmospheric corrosion as well as in acid media due to its high reactivity with oxygen and with acids. It readily suffers from corrosion in acid media so it becomes essential to protect it from corrosion in working conditions.

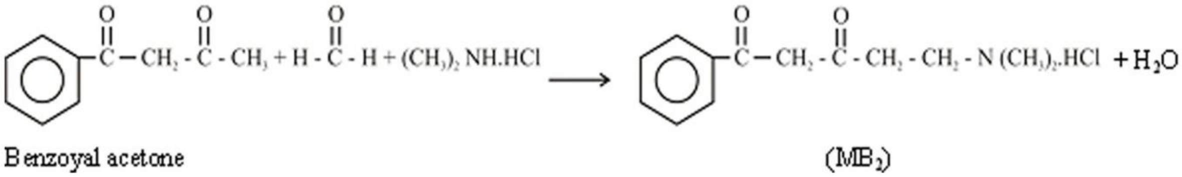
Many organic compounds have been used to prevent the corrosion of mild steel in acid media[1-3]. These compounds adsorb on metal surface and form a barrier to oxygen and moisture by complexing with metal ions or by removing corrodants from the environment, thus inhibit the corrosion. Generally the organic compounds containing heteroatom's like O, N, S are found to work as effective corrosion inhibitor[4-7]. The efficiency of these compounds depends on the electron density around the heteroatom[8]. Heteroatom's such as O, N and S are capable of forming coordinate covalent bond with metal owing to their free electron pairs. Inhibition efficiency also depends upon the number of adsorption active centres in the molecule, their charge density and molecular size, mode of adsorption and formation of metallic complexes[9].

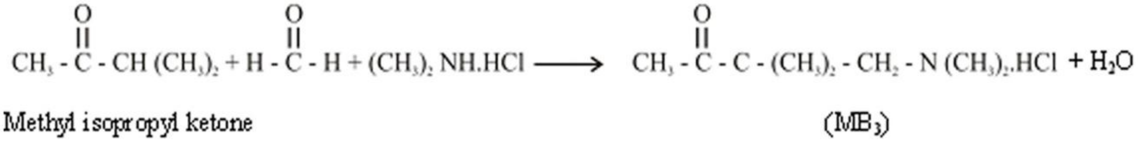
Corrosion of mild steel and its alloys in different acid media have been studied[10 & 11]. Some workers have studied corrosion inhibition efficiency of Mannich bases for mild steel in acid media[12 & 13]. Present investigation deals with the synthesis of Mannich bases and study them as corrosion inhibitor.

MATERIAL AND METHODS

Mannich bases were synthesized by conventional methods i.e. by refluxing equimolar quantities of ethanolic solutions of corresponding ketones, formaldehyde and secondary amines in a round bottom flask for about 4-5 hours and then adding some acetone in it and mixture was left in a refrigerator overnight. Resulting crystals were filtered and then recrystallized by acetone which were then dried and collected in pure state. Square shaped specimens of mild steel of dimension 2.0×2.0×0.03 cm containing a small hole of about 1mm diameter near the upper edge were used for studying the corrosion rate. Specimens were cleaned by buffing to produce a mirror finish and were then degreased. Initial weight of specimens were taken upto the three decimal of gm with a digital balance. The solutions of HCl were prepared using double distilled water.

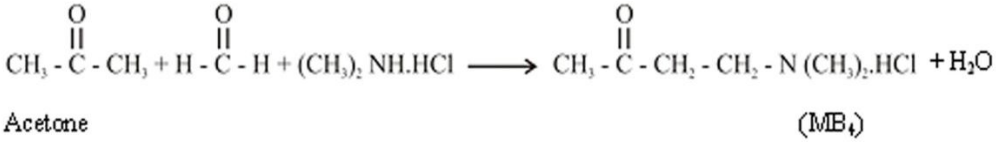






$$CH_3-\overset{\overset{O}{\|}}{C}-CH(CH_3)_2+H-\overset{\overset{O}{\|}}{C}-H+(CH_3)_2NH.HCl\longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-C-(CH_3)_2-CH_2-N(CH_3)_2.HCl+H_2O$$

Methyl isopropyl ketone (MB₃)



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3+H-\overset{\overset{O}{\|}}{C}-H+(CH_3)_2NH.HCl\longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-N(CH_3)_2.HCl+H_2O$$

Acetone (MB₄)

Each specimen was suspended by a V-shaped glass hook made up of capillary tube in a beaker containing 50 mL of the test solution at 25± 0.1°C. After the sufficient exposure, specimen was cleaned by running water and then dried by hot air dryer then final weight was taken. Duplicate experiments were performed in each case and mean values of the weight loss were determined.

The percentage inhibition efficiency (η%) was calculated as[14]:

$$\eta\% = \frac{100(\Delta W_u - \Delta W_i)}{\Delta W_u}$$

Where ΔW_u and ΔW_i are the weight loss of metal in uninhibited and in inhibited solution respectively.

The degree of surface coverage (θ) of specimen by inhibitor can be calculated as:

$$\theta = \frac{(\Delta W_u - \Delta W_i)}{\Delta W_u}$$

Inhibition efficiencies were also calculated by thermometric technique. This involved the immersion of single specimen in an insulated reaction chamber containing 50mL of solution. Initial temperature of each test solution was taken by a thermometer upto the accuracy of 0.1°C. It was observed that the temperature of the solution increased slowly initially then rapidly and attained a maximum value before falling due to exothermic nature of reaction involved in corrosion process. The maximum temperature was recorded in each case.

Percentage inhibition efficiency (η%) was calculated as[15]:

$$\eta\% = \frac{100(RN_u - RN_i)}{RN_u}$$

Where RN_u and RN_i are the reaction number in uninhibited and in inhibited solution respectively and RN (Kelvin min^{-1}) is defined as:

$$RN = \frac{(T_m - T_i)}{t}$$

Where T_m and T_i are the maximum and initial temperature of test solution respectively and t is the time (in min.) required to reach the maximum temperature.

RESULTS AND DISCUSSION

Weight loss data and inhibition efficiency (η%) for various concentrations of acid and inhibitor are given in table 1. It is clear from the table that inhibition efficiency increases with increasing concentration of inhibitor whereas it decreases with increasing concentration of acid. All the inhibitors show maximum efficiency at the lowest concentration of acid used i.e. 0.5M. Corresponding variations of inhibition efficiency with concentration of inhibitor in 0.5M HNO_3 are given in figure 1. The maximum efficiency was obtained for MB_2 at an inhibitor concentration of 400ppm in 0.5M HNO_3 i.e. 69.12%. Maximum efficiency shown by MB_2 in HNO_3 is due to the more number of atoms having high electron density which is responsible for more adsorption of inhibitor on the metal surface and decreases the rate of reaction. It is also clear from the table that inhibition efficiency decreases with increasing concentration of acid. It is because at higher concentration of oxidizing acid (HNO_3) the rate of hydrogen evolution is so large that oxygen cannot reach the metal surface which reduces the chance of formation of oxide layer on mild steel which ultimately becomes the main cause of corrosion of mild steel.

Corresponding data of Reaction Number (RN) and inhibition efficiency are given in Table 2. Thermometric experiments were carried out at higher concentrations of acid i.e. 1M, 2M and 3M because no appreciable changes of temperature were observed at lower concentrations of acid. The results indicate that reaction number decreases with increasing concentration of inhibitor whereas it increases with increasing concentration of acid. The results summarized in Table 2 show same trends as were observed in weight loss method. Although maximum efficiencies are lower as observed in thermometric method than in weight loss method. Corresponding variation of Reaction Number (RN) with concentration of inhibitor in 3N HNO_3 are shown in Figure 2.

Adsorption plays an important role in the inhibition of metallic corrosion by organic inhibitors. Generally organic molecules containing hetero atoms such as N, O, S adsorb on the metallic surface and inhibit the surface corrosion. In the case of Mannich bases N and O atoms are responsible for the adsorption. The nitrogen and oxygen atom of the Mannich bases act as the reaction centre because of its high electron density resulting in the formation of monolayer on the metal surface which decreases the rate of corrosion. Hoar and Holliday[16] exhibited that the Langmuir adsorption isotherm

$$\log [\theta /(1-\theta)] = \log A + \log C – (Q/2.303\ RT]$$

should give a straight line of unit gradient for the plot of $\log[\theta/(1-\theta)]$ versus log C, where A is a temperature independent constant, C is the bulk concentration of the inhibitor and Q is the heat liberated in electrochemical reaction. The corresponding plot shown in figure 3 is linear but the gradient is not unity. This deviation from unit behaviour can be explained on the basis of interaction among the adsorbed species on the metal surface.

It has been postulated in Langmuir adsorption isotherm that there is no interaction between the adsorbed molecules but it is not true for the organic molecules having polar groups which are adsorbed on the metal surface. These adsorbed species may interact by mutual repulsion or attraction. This is also possible for inhibitor molecules those are adsorbed on anodic and cathodic sites to interact with metallic surface as well as with each other.

Table 1: Weight loss and percentage inhibition efficiency (η%) for mild steel in HNO_3 solution with given inhibitor addition at 25± 0.1^0C; Area of specimen : $8cm^2$

Conc. of inhibitor (ppm)	**0.5M HNO_3 (180 min.)**			**1.0M HNO_3 (60 min.)**			**1.5M HNO_3 (30 min.)**			**2.0M HNO_3 (14 min.)**		
	Δw(g)	**η%**	**Logθ/1-θ**	**Δw(g)**	**η%**	**logθ/1-θ**	**Δw(g)**	**η%**	**logθ/1-θ**	**Δw(g)**	**η%**	**logθ/1-θ**
uninhibited	0.706	-		0.688	-		0.728	-		0.731	-	
MB_1												
100	0.255	63.88	0.2476	0.275	60.02	0.1764	0.302	58.51	0.1492	0.318	56.49	0.1133
200	0.248	64.87	0.2663	0.267	61.19	0.1977	0.297	59.20	0.1616	0.310	57.59	0.1328
300	0.243	65.58	0.2799	0.260	62.20	0.2162	0.285	60.85	0.1915	0.298	59.23	0.1621
400	0.240	66.00	0.2880	0.248	63.95	0.2489	0.277	61.95	0.2116	0.292	60.05	0.1769
MB_2												
100	0.242	65.72	0.2826	0.258	62.50	0.2218	0.287	60.57	0.1864	0.305	58.27	0.1449
200	0.235	66.71	0.3018	0.252	63.37	0.2380	0.278	61.81	0.2090	0.292	60.05	0.1769
300	0.232	67.13	0.3100	0.237	65.55	0.2793	0.272	62.63	0.2242	0.285	61.01	0.1944
400	0.218	69.12	0.3499	0.229	66.71	0.3018	0.258	64.56	0.2604	0.272	62.79	0.2272
MB_3												
100	0.270	61.75	0.2079	0.287	58.28	0.1451	0.308	57.69	0.1346	0.328	55.12	0.0892
200	0.262	62.88	0.2288	0.282	59.01	0.1582	0.305	58.10	0.1419	0.308	57.86	0.1376
300	0.256	63.73	0.2447	0.275	60.02	0.1764	0.299	58.92	0.1566	0.302	58.68	0.1523
400	0.250	64.58	0.2608	0.256	62.79	0.2272	0.293	59.75	0.1715	0.298	59.23	0.1621
MB_4												
100	0.285	59.63	0.1693	0.293	57.41	0.1296	0.327	55.08	0.0885	0.332	54.58	0.0797
200	0.276	60.90	0.1924	0.285	58.57	0.1503	0.318	56.31	0.1101	0.325	55.54	0.0966
300	0.270	61.75	0.2079	0.270	60.75	0.1896	0.312	57.14	0.1249	0.308	57.86	0.1376
400	0.260	63.17	0.2342	0.262	61.91	0.2109	0.297	59.20	0.1616	0.300	58.96	0.1573

Table 2: Reaction Number (RN) and inhibition efficiency (*η%*) for mild steel in HNO_3 solution with given concentration of inhibitor

Conc. of inhibitor	**1N HNO_3 (60 min.)**		**2N HNO_3 (14 min.)**		**3N HNO_3 (7 min.)**	
(ppm)	**RN($Kmin^{-1}$)**	***η%***	**RN($Kmin^{-1}$)**	***η%***	**RN($Kmin^{-1}$)**	***η%***
Uninhibited	0.1333	-	0.7142	-	2.0000	-
MB_1						
100	0.0645	51.61	0.3595	49.66	1.0515	47.42
200	0.0627	52.96	0.3520	50.71	1.0487	47.56
300	0.0595	55.36	0.3492	51.10	1.0365	48.17
400	0.0582	56.33	0.3415	52.18	1.0295	48.52
MB_2						
100	0.0612	54.08	0.3520	50.71	1.0410	47.95
200	0.0597	55.21	0.3485	51.20	1.0210	48.95
300	0.0545	59.11	0.3415	52.18	1.0120	49.40
400	0.0523	60.76	0.3350	53.09	0.9963	50.18
MB_3						
100	0.0695	47.86	0.3585	49.80	1.0690	46.55
200	0.0672	49.58	0.3545	50.36	1.0575	47.12
300	0.0658	50.63	0.3495	51.06	1.0295	48.52
400	0.0635	52.36	0.3435	51.90	1.0182	49.09
MB_4						
100	0.0735	44.86	0.3887	45.57	1.1580	42.10
200	0.0705	47.11	0.3805	46.72	1.0950	45.25
300	0.0653	51.01	0.3740	47.63	1.0895	45.52
400	0.0638	52.13	0.3692	48.30	1.0785	46.07

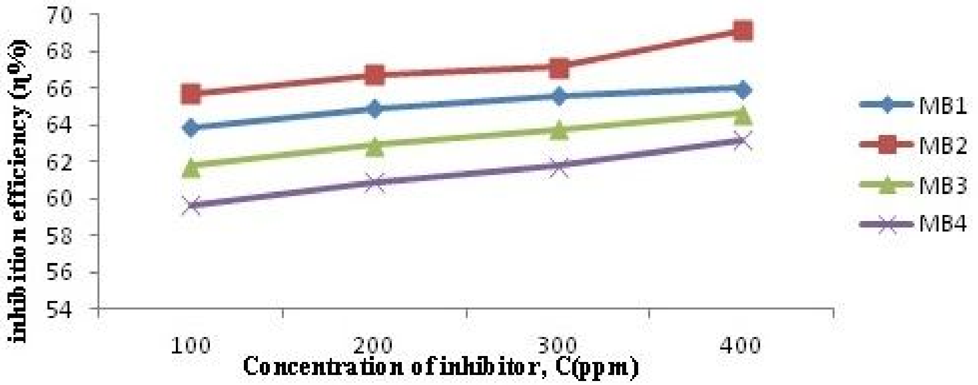


Figure 1: Variation of inhibition efficiency with concentration of inhibitor for mild steel in 0.5M HNO_3

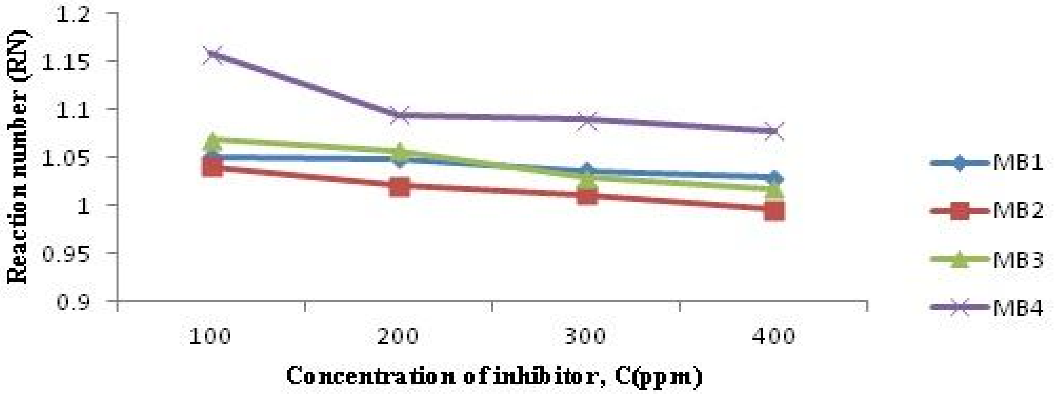


Figure 2: Variation of reaction number with concentration of inhibitor for mild steel in 3.0M HNO_3

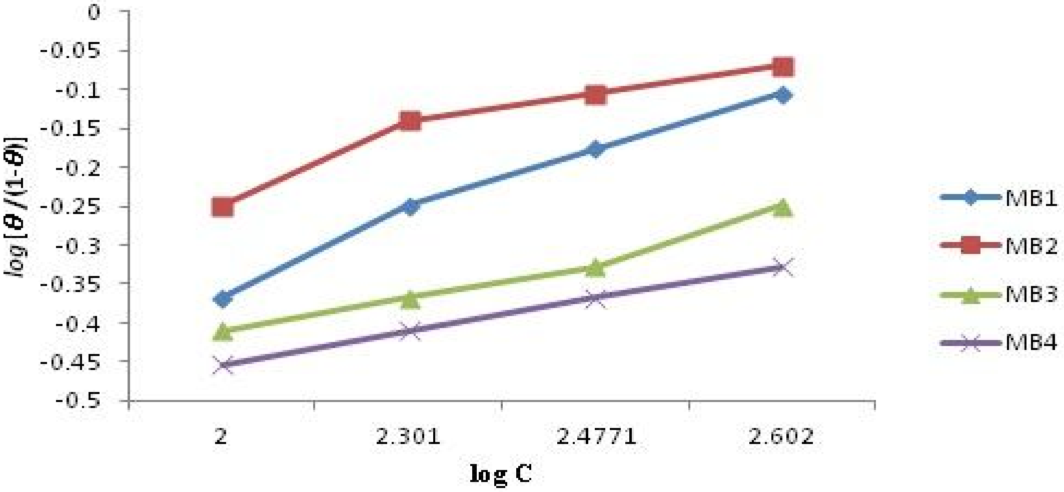


Figure 3: Langmuir adsorption isotherm for mild steel in 0.5M HNO_3

CONCLUSION

A study of four newly synthesized Mannich Bases i.e. MB_1, MB_2, MB_3 and MB_4 has shown them to be effective inhibitors for corrosion of mild steel in HNO_3 solution. Both weight loss and thermometric determination have shown that the inhibition efficiency of Mannich bases increases with increasing concentration of inhibitor whereas it decreases with increasing concentration of acid. Among the synthesized compounds under investigation the highest inhibition efficiency was shown by MB_2 at the highest concentration of inhibitor i.e. at 400 ppm in 0.5M HNO_3. So it can be concluded that newly synthesized Mannich bases have been proved to be good corrosion inhibitor for mild steel in HNO_3 solution.

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