

A Comparative Study of Corrosion Inhibition Efficiency of Some Newly Synthesised Mannich bases with Naturally Occurring Commiphora *Wightii* for Aluminium in HCl Solution

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ABSTRACT

Weight loss and thermometric methods have been used to study the corrosion inhibition efficiency of aluminium in HCl solution by naturally occurring *Commiphora wightii* and four newly synthesised Mannich bases. Results of inhibition efficiencies obtained from both methods are in good agreement with each other. Efficiencies of inhibitors increase with increasing concentration of inhibitor. The efficiencies of Mannich bases have been compared with naturally occurring *Commiphora wightii*. The efficiency of *Commiphora wightii* has been found much more than Mannich bases.

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Introduction

Pure aluminium is very soft so it is alloyed to obtain increased strength. Aluminium is having high corrosion resistance to the atmosphere and pure water due to the formation of passive oxide layer but it dissolves in HCl solution liberating H_2 gas. The corrosion of aluminium and its alloys in HCl solution has been extensively studied¹. Some Schiff's bases have also been studied as corrosion inhibitors for mild steel and aluminium in acid media of different concentrations²⁻⁵. Electron density present around the heteroatoms affects the efficiency of compounds. Inhibition efficiency also depends upon the number of adsorption active centres in the molecule, their charge density, molecular size, mode of adsorption and formation of metallic complexes. Heteroatoms such as N, O, S are capable of forming coordinate covalent bond with metal owing to their free electron pairs. Compounds with pi bonds also exhibit good inhibitive properties due to interaction of pi orbital with metal surface. Some other workers have studied corrosion inhibition efficiency of Mannich base for aluminium in HCl solution⁶⁻⁹.

In addition to the heterogenous organic compounds synthesised in laboratory some naturally occurring substances like tannin, tamarind tea leaves¹⁰, Argemone maxicana¹¹, Prosopis jolliflorar¹² have been evaluated as effective corrosion inhibitor. The naturally occurring plant products are environment friendly, compatible, nonpolluting, less toxic, easily available, biodegradable and cheaper.

Commiphora wightii easily found in Indian system. It contains several alkaloids having heteroatoms that's why the extract of different plant parts like seeds, leaves, stem root can be used as corrosion inhibitor.

In the present investigation the inhibitive effect of four newly synthesised 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) have been studied in 1M HCl solution with various concentrations of inhibitors. Inhibition efficiencies of synthesised Mannich bases have been compared with naturally occurring *Commiphora wightii*.

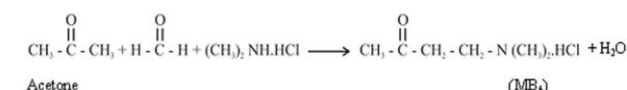
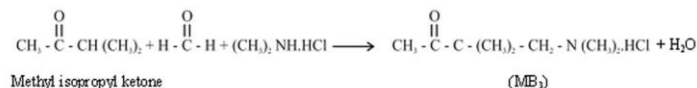
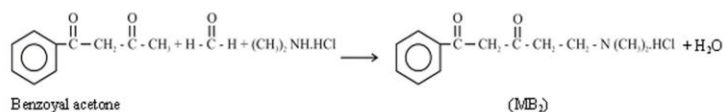
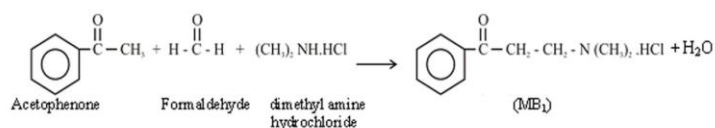
Experimental

Mannich bases were synthesised 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.

The extract of roots and leaves of *commiphora wightii* obtained by refluxing the dried leaves and roots in soxhlet in ethanol. Solutions of different concentrations of extract were prepared in ethanol.

Rectangular specimens of aluminium of dimension $2.0 \times 2.0 \times 0.03$ cm containing a small hole of about 1mm diameter near the upper edge were used for studying the corrosion rate. Initial weight of specimens were taken up to the three decimal of gm with a digital balance. The solutions of HCl were prepared using double distilled water. All chemicals used were of analytical reagent grade.

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 $25 \pm 0.1^\circ C$. 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 ($\eta\%$) was calculated as¹³:

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

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) can be calculated as¹⁴:

$$\theta = (\Delta W_u - \Delta W_i) / \Delta W_u$$

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

The corrosion rate in mm/yr is expressed as¹⁵:

$$\text{Corrosion rate (mm/yr)} = \frac{\Delta W \times 87.6}{A \times T \times D}$$

Where ΔW is the weight loss in mg, A is the area of specimen in square cm, T is the time of exposure in hours and D is the density of specimen in g/cm³.

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 ($\eta\%$) was calculated as¹⁶:

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

Where RN_u and RN_i are the reaction number in uninhibited and in inhibited solution respectively and $RN(\text{Kelvin min}^{-1})$ 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.

Result and Discussion

Weight loss data and percentage inhibition efficiency ($\eta\%$) for various concentrations of inhibitors i.e. Mannich bases and Commiphora wightii in 1M HCl are given in table1 and table 2 respectively.

Table 1. Weight loss (ΔW) and other data for aluminium in 1.0M HCl with Mannich bases

Immersion time : 2 hours

Area of specimen : 8.0cm²

Temperature : 298± 0.1K

Concentration of inhibitor C(ppm)	Weight loss ΔW (mg)	Inhibition efficiency ($\eta\%$)	Corrosion rate CR(mm/yr)	Surface coverage (θ)
uninhibited	250	-	547.50	-
MB₁				
100	95	62.00	208.05	0.6200
200	92	63.20	201.48	0.6320
300	82	67.20	179.58	0.6720
400	78	68.80	170.82	0.6880
MB₂				
100	108	56.80	236.52	0.5680
200	95	62.00	208.05	0.6200
300	90	64.00	197.10	0.6400
400	85	66.00	186.15	0.6600
MB₃				
100	110	56.00	240.90	0.5600
200	100	60.40	219.00	0.6040
300	94	62.40	205.86	0.6240
400	90	64.00	197.10	0.6400
MB₄				
100	112	55.20	245.28	0.5520
200	103	58.80	225.57	0.5880
300	97	61.20	212.43	0.6120
400	91	63.60	199.29	0.6360

Table 2. Weight loss(ΔW) and other data for aluminium in 1.0M HCl in the leaf and root extract of Commiphora wightii

Immersion time : 2 hours

Area of specimen : 8.0cm²

Temperature : 298± 0.1K

Concentration of inhibitor C(ppm)	Weight loss ΔW (mg)	Inhibition efficiency ($\eta\%$)	Corrosion rate CR(mm/yr)	Surface coverage (θ)
uninhibited	250	-	547.50	-
Leaf extract				
100	35	86.00	76.65	0.8600
200	28	88.80	61.32	0.8880
300	19	92.40	41.61	0.9240
400	07	97.20	15.33	0.9720
Root extract				
100	62	75.20	135.78	0.7520
200	52	79.20	113.88	0.7920
300	28	88.80	61.32	0.8880
400	17	93.20	37.23	0.9320

It is clear from both the tables that inhibition efficiency increases with increasing concentration of inhibitors. MB₁ shows maximum efficiency i.e.68.80% with highest concentration of inhibitor i.e. 400ppm whereas for commiphora wightii it is 97.20% for leaf extract and 93.20%

for root extract at the highest concentration of inhibitor. Corresponding variation of inhibition efficiency with the concentration of inhibitor in 1M HCl are given in figure 1.

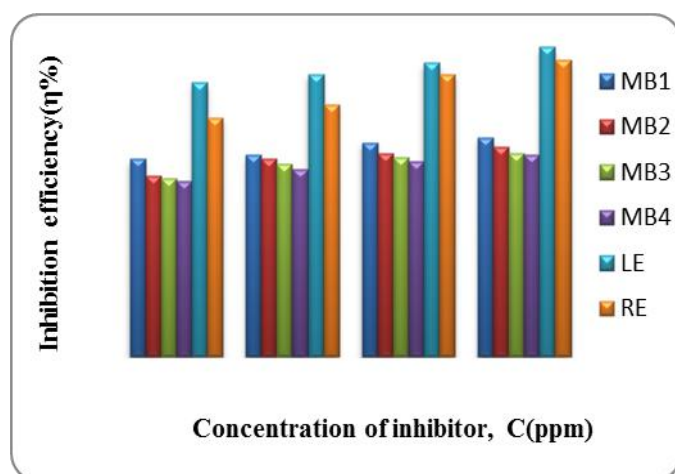


Fig 1. Variation of inhibition efficiency with concentration of inhibitors for aluminium in 1.0M HCl

Corresponding data of Reaction Number(RN) and inhibition efficiency are given in Table 3 and table 4 for Mannich bases and Commiphora wightii respectively. 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 HCl. The results indicate that reaction number decreases with increasing concentration of inhibitor. 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 3M HCl are shown in figure 2.

Table 3. Reaction number(RN) and inhibition efficiency(η%) for aluminium in HCl solution with given concentration of Mannich bases

Concentration of inhibitor C(ppm)	1.0M HCl (120 min.)		2.0M HCl (12 min.)		3.0M HCl (4 min.)	
	RN(K min ⁻¹)	(η%)	RN(K min ⁻¹)	(η%)	RN(K min ⁻¹)	(η%)
uninhibited	0.0850	-	1.0900	-	3.7500	-
MB₁						
100	0.0383	54.17	0.4080	62.56	1.1700	68.80
200	0.0341	59.88	0.3166	70.95	1.0500	72.00
300	0.0316	62.82	0.2416	77.83	0.8100	78.40
400	0.0283	66.70	0.1966	81.96	0.5900	84.26
MB₂						
100	0.0399	53.05	0.5083	53.36	1.3200	64.80
200	0.0350	58.82	0.4890	55.13	1.1300	69.86
300	0.0325	61.76	0.4057	62.77	0.9520	74.61
400	0.0301	64.58	0.2010	81.55	0.6200	83.46
MB₃						
100	0.0410	51.76	0.6012	44.84	1.9010	49.33
200	0.0361	57.52	0.4932	54.75	1.5000	60.00
300	0.0340	60.00	0.4227	61.22	1.3000	65.66
400	0.0320	62.35	0.3213	70.52	0.9400	74.93
MB₄						
100	0.0489	42.47	0.6212	43.00	2.0500	45.33
200	0.0400	52.94	0.5225	52.06	1.6010	57.33
300	0.0350	58.82	0.4321	60.35	1.4500	61.33
400	0.0330	61.17	0.3987	63.42	1.1520	69.33

Table 4. Reaction number(RN) and inhibition efficiency(η%) for aluminium in HCl solution in leaf and root extract of Commiphora wightii

Concentration of inhibitor C(ppm)	1.0M HCl (120 min.)		2.0M HCl (12min.)		3.0M HCl (4 min.)	
	RN(K min ⁻¹)	(η%)	RN(K min ⁻¹)	(η%)	RN(K min ⁻¹)	(η%)
uninhibited	0.0850	-	1.0900	-	3.7500	-
Leaf Extract						
100	0.0245	71.17	0.2416	77.83	0.7100	81.06
200	0.0205	75.88	0.1916	82.42	0.5900	84.26
300	0.0111	86.94	0.1330	87.79	0.4100	89.06
400	0.0080	90.58	0.0850	92.20	0.2560	93.17
Root Extract						
100	0.0265	68.82	0.2650	75.68	0.8253	77.99
200	0.0245	71.17	0.2110	80.64	0.6990	81.36
300	0.0218	74.35	0.1930	82.29	0.5225	86.06
400	0.0190	77.64	0.1450	86.69	0.4330	88.45

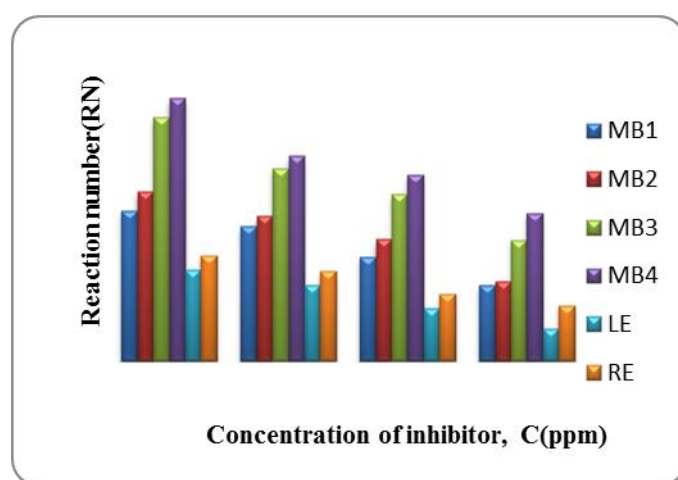


Fig 2. Variation of reaction number with concentration of inhibitors for aluminium in 3.0M HCl

Corrosion inhibition efficiency of Mannich bases and Commiphora wightii is based on the phenomenon of adsorption. Mannich bases containing heteroatoms like N and in some cases O, S get adsorbed on the surface of metals. Hetero atoms like N, O, S which have higher electron density get adsorbed more tightly on the surface of metal due to strong interactions with metallic molecules and thus blocking the active centers on the metallic surface for electrochemical reaction taking place during corrosion. More the surface coverage by Mannich base, less will be the availability of active sites on the surface and consequently less will be the corrosion rate.

Conclusions

A study of four newly synthesised Mannich bases i.e. MB₁, MB₂, MB₃ and MB₄ and Commiphora wightii has shown them to be effective inhibitors for corrosion of aluminium in HCl solution. Both weight loss and thermometric determination have shown that the inhibition efficiency of Mannich bases and Commiphora wightii increases with increasing concentration of inhibitor. A comparison between the inhibition efficiency of synthesized Mannich bases and Commiphora wightii has shown that leaf extract of Commiphora wightii is better corrosion inhibitor than Mannich bases.

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