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A comparative study of corrosion inhibitive efficiency of some newly synthesized Mannich bases with their parent amine for Al in HCl solution

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Abstract

Weight loss and thermometric methods have been used to study the corrosion inhibition of aluminium in HCl solution by 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). Results of inhibition efficiencies obtained from both methods are in good agreement with each other. Efficiency of inhibitor increases with increasing concentration of inhibitor as well as that of HCl solution. The efficiencies have been compared with those of parent amine from which Mannich bases have been derived. Inhibition efficiencies of synthesized Mannich bases have been found much more than their parent amine. It was observed that inhibition efficiencies of amine increases with increasing concentration of amine whereas it decreases with increasing concentration of acid.

Keywords: Efficiency, corrosion rate, reaction number, weight loss, Mannich base.

Introduction

Aluminium is a metal of an industrial importance. Since pure aluminium is soft and weak so it is alloyed to obtain increased strength. Aluminium is a light metal having good corrosion resistance to atmosphere and pure water but it is corroded adversely in the presence of aqueous solution of acids. It dissolves in acids liberating H_2 gas. The corrosion of aluminium and its alloys in HCl solution has been extensively studied[1]. Some Schifff's bases have also been studied corrosion inhibitors for mild steel and aluminium in acid media of different concentrations[2-5]. The efficiency of these compounds depends upon the electron density present around the heteroatoms. 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 solution[6-12].

In the present investigation the inhibitive effect of 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) have been studied in different strength of HCl solution with various concentrations of inhibitors.Inhibition efficiencies of synthesized Mannich bases have been compared with their parent amine.

Material and Methods

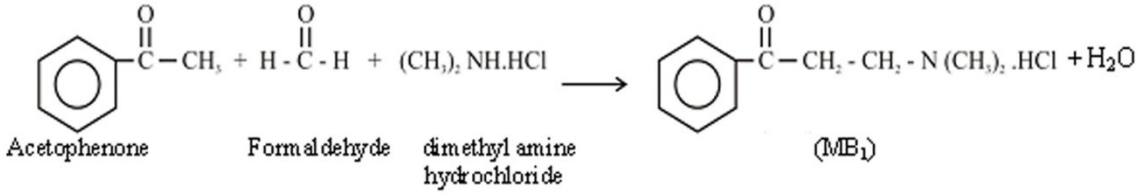
Mannich bases were synthesised by conventional methods i.e. by refluxing equimolar quantities of ethanolic solutions of corresponding ketones, formaldehyde and secondary amines in a round bottom flask for about 4-5 hours and then adding some acetone in it and mixture was left in a refrigerator overnight. Resulting crystals were filtered and then recrystallized by acetone which were then dried and collected in pure state.

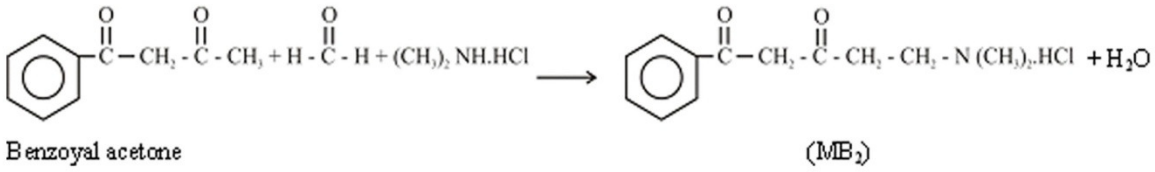
Rectangular specimens of aluminium of dimension 2.0×2.0×0.03 cm containing a small hole of about 1mm diameter near the upper edge were used for studying the corrosion rate. Specimens were cleaned by buffing to produce a mirror finish and were then degreased. Intial weight of specimens were taken upto the three decimal of gm with a digital balance. The solutions of HCl were prepared using double distilled water. All chemicals used were of analytical reagent grade.

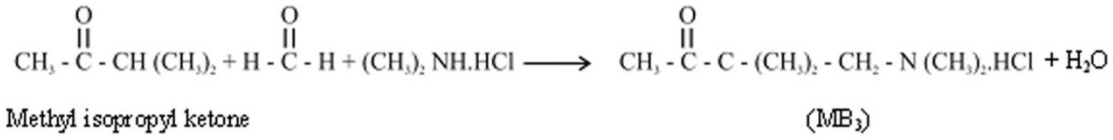
Each specimen was suspended by a V-shaped glass hook made up of capillary tube in a beaker containing 50 mL of the test solution at 25 ± 0.1°C. After the sufficient exposure, specimen was cleaned by running water and then dried by hot air dryer then final weight was taken.

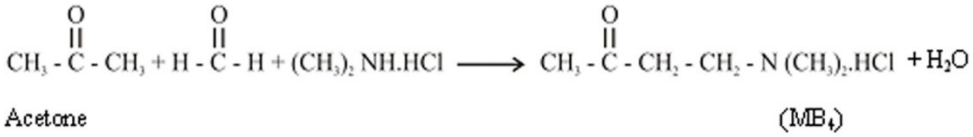
Duplicate experiments were performed in each case and mean values of the weight loss were determined. The percentage inhibition efficacy (η%) was calculated as[13]:

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









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 as[14] :
$\theta = (\Delta W_u - \Delta W_i) / \Delta W_u$
Where Δw_u and Δw_i are the weight loss of the metal in uninhibited and in inhibited solution respectively.

Inhibition efficacies 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 efficacy (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 percentage inhibition efficacy (η%) for various concentrations of acid and inhibitor are given in table1. It is clear from the table that inhibition efficacy increases with increasing concentration of inhibitor as well as that of acid. It is also evident from the table that all inhibitor show maximum efficiency at the highest concentration of acid used i.e. 2N. MB_1 and MB_2 show almost same efficiency in 2N HCl with highest concentration of inhibitor i.e. 400ppm.Corresponding variation of inhibition efficiency with the concentration of inhibitor in 2N HCl are given in figure 1.

Table-1
Weight loss (ΔW) and inhibition efficiency (*η%*) for aluminum in HCl solution with given concentration of inhibitor

Conc.of inhibitor	0.5 N HCl (72hrs.)				1N HCl (120min.)				1.5 N HCl (20min.)				2N HCl (12min.)			
(ppm)	ΔW (mg)	I.E. (η%)	θ	$\log \frac{\theta}{1-\theta}$	ΔW (mg)	I.E. (η%)	θ	$\log \frac{\theta}{1-\theta}$	ΔW (mg)	I.E. (η%)	θ	$\log \frac{\theta}{1-\theta}$	ΔW (mg)	I.E. (η%)	θ	$\log \frac{\theta}{1-\theta}$
Uninhibited	185	-	-	-	250		_	_	271	_	_	_	269	_	_	_
MB_1																
100	76	58.91	0.5891	0.1564	95	62.00	0.6200	0.2125	90	66.78	0.6678	0.3032	72	73.23	0.7323	0.4370
200	70	62.16	0.6216	0.2155	92	63.20	0.6320	0.2348	80	70.47	0.7047	0.3791	56	79.18	0.7918	0.5801
300	62	66.48	0.6648	0.2973	82	67.20	0.6720	0.3114	65	76.01	0.7601	0.5008	48	82.15	0.8215	0.6629
400	60	67.56	0.6756	0.3186	78	68.80	0.6880	0.3434	50	81.54	0.8154	0.6451	22	91.82	0.9182	1.0224
MB_2																
100	80	56.75	0.5675	0.1179	108	56.80	0.5680	0.1188	115	57.56	0.5756	0.1323	95	64.68	0.6468	0.2627
200	75	59.45	0.5945	0.1661	100	60.40	0.6040	0.1833	97	64.20	0.6420	0.2536	65	75.83	0.7583	0.4965
300	70	62.16	0.6216	0.2155	90	64.00	0.6400	0.2498	71	73.80	0.7380	0.4497	58	78.43	0.7843	0.5606
400	64	65.40	0.6540	0.2764	85	66.00	0.6600	0.2880	68	74.90	0.7490	0.4747	24	91.07	0.9107	1.0085
MB_3																
100	82	55.65	0.5565	0.0985	110	56.00	0.5600	0.1047	112	58.67	0.5867	0.1521	108	59.85	0.5985	0.1733
200	80	56.75	0.5675	0.1179	100	60.40	0.6040	0.1833	103	61.99	0.6199	0.2124	100	62.96	0.6296	0.2303
300	75	59.45	0.5945	0.1661	94	62.40	0.6240	0.2199	90	66.78	0.6678	0.3032	87	67.65	0.6765	0.3203
400	70	62.16	0.6216	0.2155	90	64.00	0.6400	0.2498	72	73.43	0.7343	0.4414	69	74.34	0.7434	0.4619
MB_4																
100	91	50.65	0.5065	0.0112	112	55.20	0.5520	0.0996	120	55.71	0.5571	0.0996	112	58.36	0.5836	0.1465
200	82	55.65	0.5565	0.0985	103	58.80	0.5880	0.1455	113	58.30	0.5830	0.1455	106	60.59	0.6059	01867
300	80	56.75	0.5675	0.1179	97	61.20	0.6120	0.2890	92	66.05	0.6605	0.2890	90	66.54	0.6654	0.2985
400	78	57.83	0.5783	0.1371	91	63.60	0.6360	0.3777	80	70.47	0.7047	0.3777	76	71.74	0.7174	0.4045

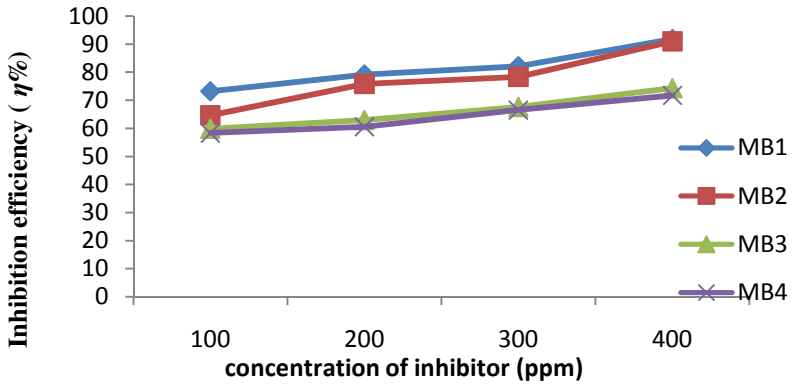


Figure-1: Variation of inhibition efficiency with concentration of inhibitor for aluminium in 2N HCl

Corresponding data of Reaction Number (RN) and inhibition efficacy are given in Table 2. Thermometric experiments were carried out at higher concentrations of acid i.e. 1N, 2N and 3N 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 as well as that of acid. 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 HCl are shown in figure 2.

Table-2

Reaction Number (RN) and inhibition efficacy (η%) for aluminum in HCl solution with given concentration of inhibitor

Conc. of inhibitor	1N HCl (120 min.)		2N HCl (12 min.)		3N HCl (4 min.)	
(ppm)	RN($Kmin^{-1}$)	η%	RN($Kmin^{-1}$)	η%	RN($Kmin^{-1}$)	η%
Uninhibited	0.085	_	1.09	_	3.75	_
MB_1						
100	0.0383	54.17	0.0408	62.54	1.170	68.80
200	0.0341	59.88	0.3166	70.95	1.050	72.00
300	0.0316	62.82	0.2416	77.83	0.810	78.40
400	0.0283	66.70	0.1966	81.96	0.590	84.26
MB_2						
100	0.0399	53.05	0.5083	53.36	1.320	64.80
200	0.0350	58.82	0.4890	55.13	1.130	69.86
300	0.0325	61.76	0.4057	62.77	0.952	74.61
400	0.0301	64.58	0.2010	81.55	0.620	83.46
MB_3						
100	0.0410	51.76	0.6012	44.84	1.901	49.33
200	0.0361	57.52	0.4932	54.75	1.500	60.00
300	0.0340	60.00	0.4227	61.22	1.300	65.66
400	0.0320	62.35	0.3213	70.52	0.940	74.93
MB_4						
100	0.0489	42.47	0.6212	43.00	2.050	45.33
200	0.0400	52.94	0.5225	52.06	1.601	57.33
300	0.0350	58.82	0.4321	60.35	1.450	61.33
400	0.0330	61.17	0.3987	63.42	1.152	69.33

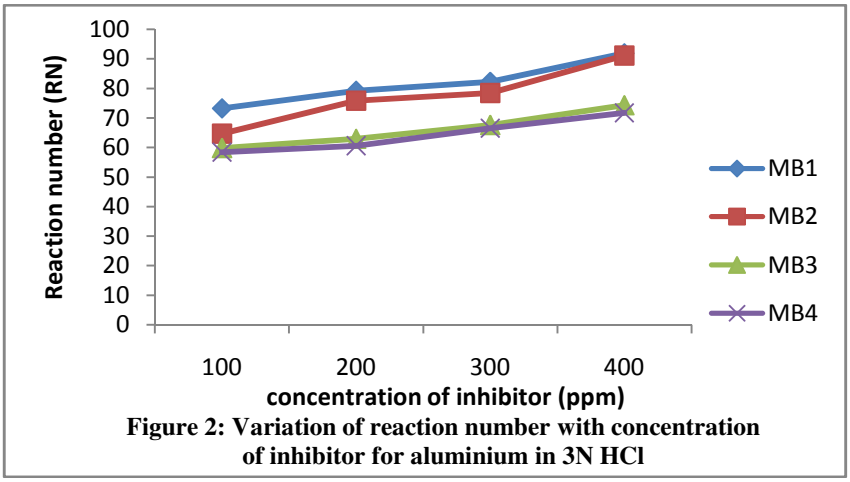


Figure 2: Variation of reaction number with concentration of inhibitor for aluminium in 3N HCl

Corrosion inhibition efficiency of Mannich bases 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 according to Langmuir adsorption. 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. Presence of phenyl group on MB_1 and MB_2 further enhanced the electron density which ultimately decreases the active sites and thus increases the corrosion inhibition efficiency of MB_1 and MB_2. That is why, MB_1 and MB_2 show higher percentage of inhibition efficacy in comparison to MB_3 and MB_4. It has also been observed that efficiency of inhibitors increase on increasing concentration of HCl.

Table-3

Weight loss (ΔW) and inhibition efficacy ($\eta\%$) for aluminum in HCl solution with parent amine (DMA)

Temperature: 25 ± 0.1^{0}C, Area of specimen: 8cm^2

Conc. of inhibitor	0.5 N HCl (72hrs.)				1N HCl (120min.)				1.5 N HCl (20min.)				2N HCl (12min.)			
(ppm)	ΔW (mg)	I.E. (η%)	θ	$\log \frac{\theta}{1-\theta}$	ΔW (mg)	I.E. (η %)	θ	$\log \frac{\theta}{1-\theta}$	ΔW (mg)	I.E. (η%)	θ	$\log \frac{\theta}{1-\theta}$	ΔW (mg)	I.E. (η%)	θ	$\log \frac{\theta}{1-\theta}$
Uninhibited	185	–	–	–	250	–	–	–	271	–	–	–	269	–	–	–
DMA																
100	110	40.54	0.4054	-0.1663	153	38.80	0.3880	-0.1979	207	23.61	0.2361	-0.5100	234	13.01	0.1301	-0.8253
200	90	51.35	0.5135	0.0234	127	49.92	0.4992	-0.0013	201	25.83	0.2583	-0.4581	205	23.79	0.2379	-0.5057
300	82	55.67	0.5567	0.0989	116	53.60	0.5360	0.0626	167	38.37	0.3837	-0.2058	171	36.43	0.3643	-0.2418
400	78	57.83	0.5783	0.1371	111	55.60	0.5560	0.0976	164	39.48	0.3948	-0.1855	165	38.66	0.3866	-0.2005

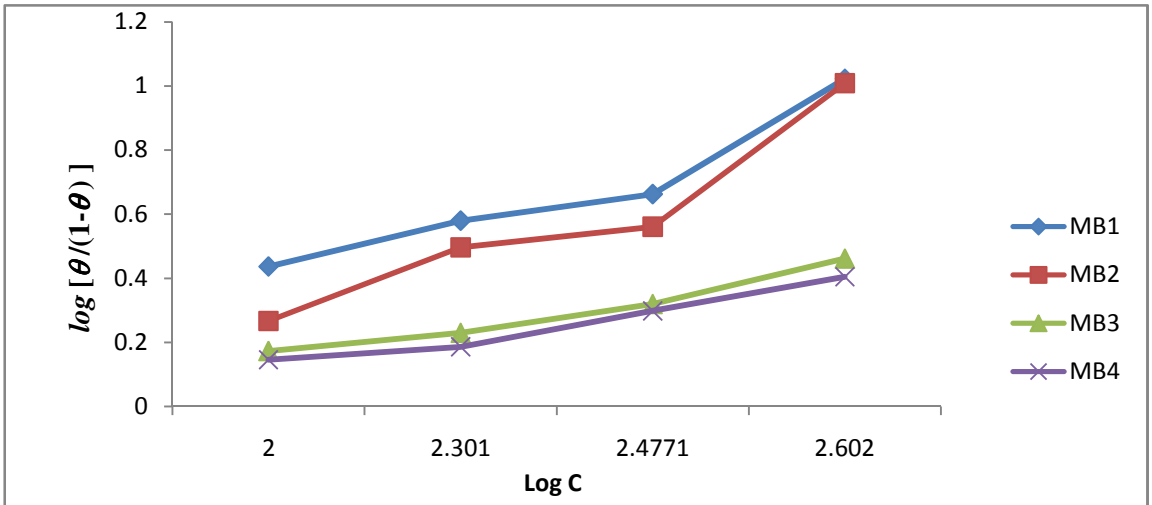


Fig 3: Langmuir Adsorption Isotherm for aluminium in 2N HCl

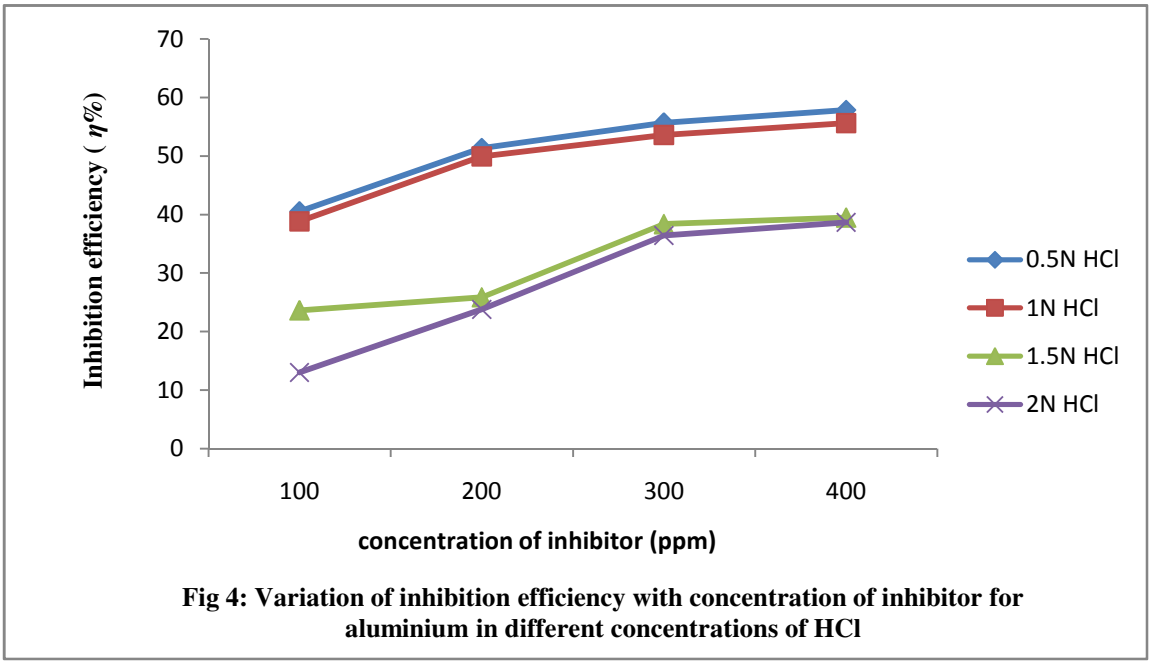


Fig 4: Variation of inhibition efficiency with concentration of inhibitor for aluminium in different concentrations of HCl

The probable reason of this may be due to the more ionization of Mannich bases in more acidic strength. Hoar and Holliday have used the Langmuir adsorption isotherm to study inhibition charteristics, assuming that inhibitors adsorbed on the metal surface decrease the surface area available for cathodic and anodic reaction using following equation[16].

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

This equation should give a straight line of unit gradient for the plot of $log\ [\theta/(1-\theta)\ ]$ v/s $log\ C$, where A is the temperature independent constant, C is the bulk concentration of the inhibitor and Q is the heat evolved during the adsorption.

The corresponding plots between $log\ [\theta/(1-\theta)\ ]$ and $log\ C$ shown in fig.3 for aluminium in 2N HCl. The plots are linear but gradients are not equal to unity as would be expected for the ideal Langmuir adsorption isotherm equation. This deviation from unity may be explained on the basis of the interaction among the adsorbed species on the metal surface. It has been postulated in the derivation of the Langmuir isotherm equation that the adsorbed molecule do not interact with one another and form a monolayer on the metal surface but practically this is not possible in the case of organic molecules having polar atoms or groups which are adsorbed on the anodic and cathodic sites of the metal. Such adsorbed species may interact by mutual repulsion or attraction. This phenomenon is also possible for present inhibitor molecules those are adsorbed on anodic and cathodic sites to interact with metallic surface as well as with each other so they may not form monolayer on the surface of metal which may be a possible cause of deviation from unit gradient.

A comparison was made between the synthesized Mannich bases and their parent amine i.e. dimethyl amine. The results for the parent amine have been summarized in table 3 for HCl. It was found that maximum efficiency is 57.83% in 0.5N HCl. It can been observe from the table that inhibition efficiency of amine decreases with increasing concentration of acid. Corresponding variation of inhibition efficiency with the concentration of inhibitor in different concentrations of HCl are given in figure 4.

Conclusions

A study of four newly synthesised Mannich bases i.e. MB_1, MB_2, MB_3 and MB_4 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 increases with increasing concentration of acid and that of inhibitor. Among the synthesised inhibitors under investigation the highest inhibition efficacy was shown by MB_1 and MB_2 at the highest concentration of inhibitor i.e. at 400 ppm. A comparison between the inhibition efficiency of synthesized Mannich bases and their parent amine has shown that synthesized Mannich bases are better corrosion inhibitor than parent amine.

It has also observed that Langmuir adsorption isotherm deviate somewhat from their ideal behavior. This is attributed to the fact that adsorbed molecules interact with each other causing deviation in the behavior of Langmuir adsorption isotherm.

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