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Efficacy of some newly synthesised mannich bases as corrosion inhibitor on aluminium in HCl solution

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ABSTRACT

Weight loss, thermometric and potentiometric methods have been used to study the corrosion inhibition of aluminum 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 efficacies obtained from said methods are in good agreement with each other. Efficacy of inhibitor increases with increasing concentration of inhibitor as well as that of HCl solution.

Introduction

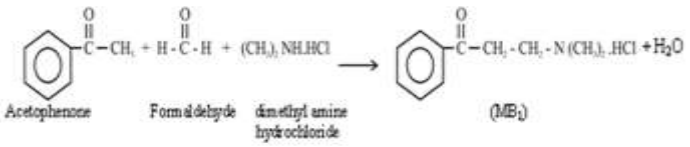
Aluminium being an industrially important metal is subjected to corrosion in service by various corrosion agents among which the aqueous acids are most dangerous. Since pure aluminium is soft and weak so it is alloyed to obtain increased strength. Aluminium is a light metal having good corrosion resistance 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[1-4]. Some Schifff's bases have also been studied corrosion inhibitors for mild steel and aluminium in acid media of different concentrations[5-7].Some other workers have studied corrosion inhibition efficiency of Mannich base for aluminium in HCl solution[8-13].

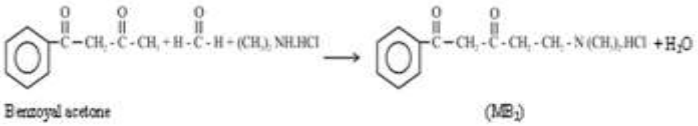
In the present investigation the inhibitive effect of four newly synthesized Mannich bases viz 3-oxo, 3-phenyl, N,N-dimethyl propanamine hydrochloride (MB_1), 3,5-dioxo,5-phenyl N,N-dimethyl pentanamine hydrochloride(MB_2), 2,2-dimethyl,3-oxo N,N dimethyl butanamine hydrochloride (MB_3) and 3-oxo N,N-dimethyl butanamine hydrochloride((MB_4) have been studied in different strength of HCl solution with various concentrations of inhibitors.

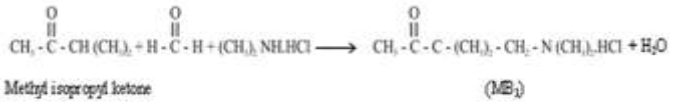
Experimental

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.

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. 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. 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

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performed in each case and mean values of the weight loss were determined.

The percentage inhibition efficacy (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.

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 .

Potentiometric studies were also performed for the same specimen. In this study potential of test solutions were recorded at regular intervals using highly précised millivoltmeter cum pH meter during the exposure of specimen in corrosive media i.e. in HCl with and without inhibitors .

Result and discussion

Weight loss experiment

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 display 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 efficacy with the concentration of inhibitor in 2N HCl are given in figure 1.

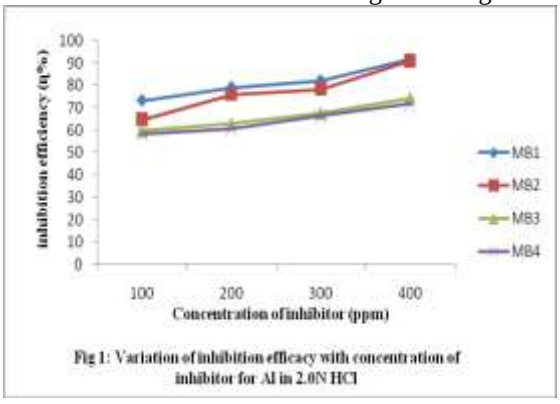

Fig 1: Variation of inhibition efficacy with concentration of inhibitor for Al in 2.0N HCl

Thermometric experiment

Corresponding data of Reaction Number(RN) and inhibition efficacy are given in Table2. 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. The results summarized in table2 show same trends as were observed in weight loss method. Although maximum efficacies 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.

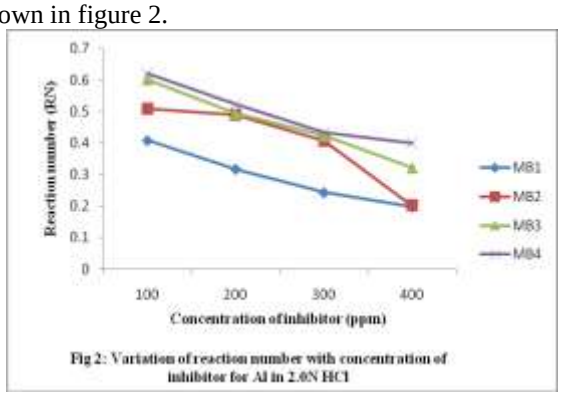

Fig 2: Variation of reaction number with concentration of inhibitor for Al in 2.0N HCl

Electrochemical experiment

The variation of electrode potential of different test solutions were also taken into account with and without inhibitor. The observed variation of potentials with time for MB_1 in 2N HCl are shown in figure 3.The trends show that potential with time increases in each case as the reaction goes on.

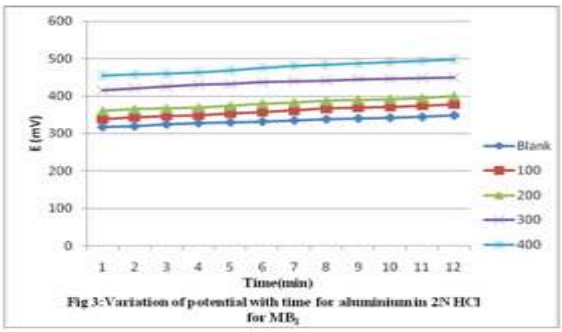

Fig 3:Variation of potential with time for aluminium in 2N HCl for MB_1

The molecules having heteroatoms like O,N,S etc.which have lone pair of electrons form a protective layer on the surface of the metal due to Langmuir monolayer adsorption which deactivate the active centres on the metal, thus retards the electrochemical reaction occurring during the process of corrosion. More the number of atoms with high electron density attached to the inhibitor more is the inhibition efficacy. In present study all the synthesized Mannich bases have two atoms of higher electron density i.e. O and N due to which these Mannich bases get adsorbed on the surface of aluminium and form a protective layer. Presence of phenyl group on MB_1 and MB_2 further enhanced the electron density which ultimately increases the corrosion inhibition efficacy. 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 efficacy of inhibitors increases on increasing concentration of HCl. The probable reason for this observation may be attributed to the fact that Mannich bases are more active in more acidic strength due to a simple phenomenon of acid-base reaction.

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 efficacy of Mannich bases increases with increasing concentration of acid and inhibitor. Among the synthesised compounds 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. So it can be concluded that newly synthesized Mannich bases have been proved to be good corrosion inhibitor for aluminium in HCl solution.

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Table1 Weight loss(ΔW) and inhibition efficacy (*η%*) for aluminium in HCl solution with given concentration of inhibitor

Temperature : 25 ± 0.1^{0}C				Area of specimen :8cm^2				
Conc. of inhibitor	0.5 N HCl (72 hrs.)		1N HCl (120 min.)		1.5N HCl (20 min.)		2N HCl (12 min.)	
(ppm)	Δw (g)	*η%*	Δw (g)	*η%*	Δw (g)	*η%*	Δw (g)	*η%*
Uninhibited	0.185	_	0.250	_	0.271	_	0.269	_
MB_1								
100	0.076	58.91	0.095	62.00	0.090	66.78	0.072	73.23
200	0.070	62.16	0.092	63.20	0.080	70.47	0.056	79.18
300	0.062	66.48	0.082	67.20	0.065	76.01	0.048	82.15
400	0.060	67.56	0.078	68.80	0.050	81.54	0.022	91.82
MB_2								
100	0.080	56.75	0.108	56.80	0.115	57.56	0.095	64.68
200	0.075	59.45	0.100	60.40	0.097	64.20	0.065	75.83
300	0.070	62.16	0.090	64.00	0.071	73.80	0.058	78.43
400	0.064	65.40	0.085	66.00	0.068	74.90	0.024	91.07
MB_3								
100	0.082	55.65	0.110	56.00	0.112	58.67	0.108	59.85
200	0.080	56.75	0.100	60.40	0.103	61.99	0.100	62.96
300	0.075	59.45	0.094	62.40	0.090	66.78	0.087	67.65
400	0.070	62.16	0.090	64.00	0.072	73.43	0.069	74.34
MB_4								
100	0.091	50.65	0.112	55.20	0.120	55.71	0.112	58.36
200	0.082	55.65	0.103	58.80	0.113	58.30	0.106	60.59
300	0.080	56.75	0.097	61.20	0.092	66.05	0.090	66.54
400	0.078	57.83	0.091	63.60	0.080	70.47	0.076	71.74

Table2 Reaction Number (RN) and inhibition efficacy ($\eta\%$) for aluminium 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($Kmin^{-1}$)	$\eta\%$	RN($Kmin^{-1}$)	$\eta\%$	RN($Kmin^{-1}$)	$\eta\%$
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