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Study of corrosion inhibition efficiency of newly synthesized Schiff's bases on Aluminium in HCL solution

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ABSTRACT

Corrosion inhibition efficiency of newly synthesized Schiff's bases viz. *N-(4-N,N' dimethyl amino benzal)-1- naphthyl amine* (SB_1), *N-(4-methoxy benzal)-1-naphthyl amine* (SB_2) and *N-(4-methoxy benzal)-2- amino pyridine* (SB_3) for aluminium in HCl solution was studied using weight loss, potentiometric and thermometric methods. Inhibition efficiency was found to be increase with increasing concentration of inhibitor as well as with acid strength. Results obtained by all methods have been found in good agreement with each other. Results revealed that SB_2 is better corrosion inhibitor than SB_1 and SB_3. Maximum efficiency was found 99.23% in 2.5N HCl solution for 0.4% concentration of SB_2.

Introduction

Aluminium is soft, durable, light weight, malleable and nonmagnetic metal with appearance ranging from silvery to dull grey depending upon the surface roughness. It has higher strength/weight ratio and about 1/3 the density and stiffness than steel, which makes it a major component of structural material for aircrafts, transports, internal outfits for industries and other engineering uses [1].

Aluminium has excellent corrosion resistance due the formation of thin surface layer of aluminium oxide, which effectively preventing further oxidation, when metal is exposed to air. The resistance towards corrosion becomes less for alloyed aluminium due to galvanic reactions. Thus alloy of aluminium are recommended for building purpose. These alloys have good resistance to concretes, mortors, plasters, and asbestos and cement products [2]. Aluminium has face centered cubic structure [3,4] due to which it has resistance to brittle cleavage fracture at low temperature, this enables aluminium to be used for making tanks and vessels to hold reactants and products at very low temperature.

The corrosion resistance is reduced greatly when many aqueous salts are present particularly in the presence of dissimilar metals. Thus aluminium is not attacked by pure water but dissolves in aqueous solutions of acids. In acidic medium hydrogen evolution reaction predominates.

$$2\,Al + 6\,HCl + 12\,H_2O \rightarrow 2\,[Al(H_2O)_6]Cl_3 + 3\,H_2\uparrow$$

In addition to naturally occurring plants [5], many heterogeneous organic compounds like Schiff's bases[6,7], Mannich bases[8-10], Thio compounds[11] have been studied as effective corrosion inhibitors for many metals including aluminium. Heterogeneous organic compounds containing atoms of high electron density like N, O, S, P and sometimes Se are resistive to corrosion effectively due to high electron density and high basicity. The effectiveness of inhibition depends upon charge density around hetero atom, number of adsorption active centers, size, shape, and orientation of inhibitor molecule[12]. These inhibitors get adsorbed on the surface of metal and block the discharge of H^+ ions and dissolution of metal ion. Schiff's bases show excellent inhibitive characteristics due to presence of π bond in imine linkage.

The inhibitive nature of Schiff's bases increases due to interaction of π orbital with metal surface and complexing behaviour towards metal ion.

A large number of Schiff's base complexes of transition metals have been synthesized and evaluated for biological activities. They are also used as antiviral [13], anti HIV [14], anti malarial [15], anti microbial [16], anti inflammatory [17], anti leukemic [18] and anti cancer agents [19]. Schiff's bases have also been extensively studied as radio protective moieties [20] and effective corrosion inhibitors [21].

Experimental

Present investigation deals with the study of rate of corrosion of metals and inhibition efficiency of newly synthesized Schiff's bases viz. *N-(4-N,N' dimethyl amino benzal)-1- naphthyl amine* (SB_1), *N-(4-methoxy benzal)-1-naphthyl amine* (SB_2) *and N-(4-methoxy benzal)-2- amino pyridine* (SB_3) for aluminium in HCl solution using weight loss, potentiometric and thermometric methods.

In weight loss method aluminium sheet of high grade purity (AR grade) was taken and cleaned by an emery paper with no spot on the sheet and degreased with acetone to remove all greasy material from the sheet. Specimen samples of dimension 2cm.×2cm. with thickness 0.03 cm. were cut from the center of the sheet. A small hole of about 2mm. diameter near the upper edge of the specimen was made by a sharp hard needle and initial weight of each specimen was taken with a digital balance with accuracy of 0.001 g. The solutions of inhibitors were prepared in ethanol and solutions of HCl were prepared using double distilled water with AR grade of chemicals.

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Specimens were plunged in 50 mL test solution (HCl) using a V- shaped glass hook prepared by capillary at room temperature. After sufficient time of exposure, specimens were cleaned with running water, dried using hot air dryer and then final weight of each specimen was taken. Duplicate observations were made to minimize the error. Inhibition efficiency was calculated using the formula [22]

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

Where, ΔW_u = Weight loss of specimen in uninhibited solution.

ΔW_i = Weight loss of specimen in inhibited solution

Inhibition efficiency was also calculated by thermometric method. The specimens were immersed in test solution in an insulated chamber with a thermometer of accuracy of 0.1°C and initial temperature was noted. As the reaction started, initially the temperature of reaction increased slowly then rapidly and after attaining a maximum value, it decreased. The maximum temperature was noted and inhibition efficiency was calculated as [23]

$$\eta\% = \left(\frac{RN_f - RN_i}{RN_f}\right) \times 100$$

Where RN_f = Reaction Number in free solution.

RN_i = Reaction Number in inhibited solution.

Reaction number was calculated as [24]

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

Where T_m and T_i are maximum and initial temperatures respectively and t is the time in minutes required to reach maximum temperature.

Corrosion rate in mm/yr was calculated as[25]:

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

Where ΔW = Weight loss in mg.

T = Time (in hours) of exposure of specimen in solution.

A = Exposed area of metal surface in cm^2.

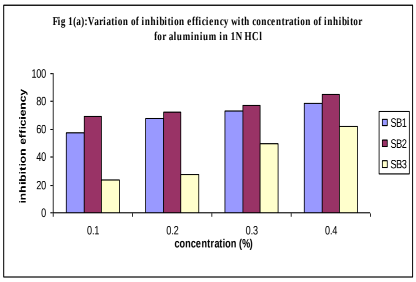
D = Density of specimen in gcm^{-3}.

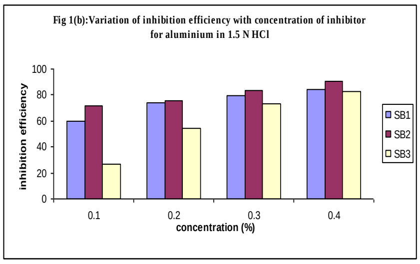
In potentiometric method the variation of potential difference with time in 2.5M HCl for different concentrations of all the three synthesized Schiff's bases were observed.

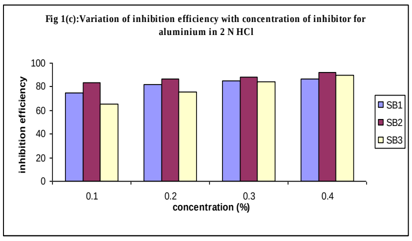
Results And Discussion

Weight loss, reaction number data and corresponding values of inhibition efficiencies and corrosion rate are given in table-1 and table-2 respectively. Results shown in table-1 indicate that inhibition efficiency increases with increasing concentration of inhibitor and it also increases with increasing acid strength. Maximum inhibition efficiency (99.23%) was found at maximum concentration (2.5N HCl) of acid as well as that of inhibitor (0.4%). Inhibition efficiency increases with increasing acid strength due to the fact that at higher concentration of acid more dissociation of inhibitor i.e. Schiff's base occurs thus, it absorbed more on the metal surface and decrease the active centers and exposed area on the surface of metal.

Among all the three inhibitors SB_2 shows highest efficiency due to the presence of methoxy ($-OCH_3$) group which enhances electron density on active site. It is due to the fact that inhibition efficiency of inhibitor depends on electron density around hetero atom, as electron density increases inhibition efficiency increases. Corresponding variations of inhibition efficiencies with concentration of inhibitor are shown in fig.1 (a) to fig.1 (d) for different concentrations of HCl solution.







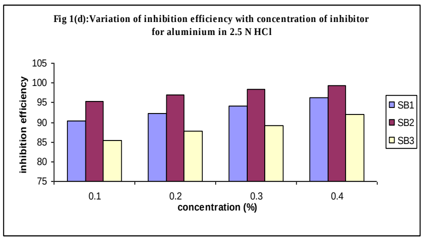


Table-2 shows the corresponding data of reaction number with different concentration of inhibitor in 1N, 2N and 3N concentrations of HCl solution. It was observed that at lower concentration of HCl there were no appreciable changes in temperature, so higher concentrations of HCl were taken. Corresponding curve for the variation of reaction number with concentration of inhibitor is shown in fig.2 for highest concentrations (3N) of HCl solutiuon. Results indicate that reaction number decreases with increasing concentration of inhibitor and increases with increasing concentration of acid. Results for inhibition efficiency show same trend in thermometric method as observed by weight loss method.

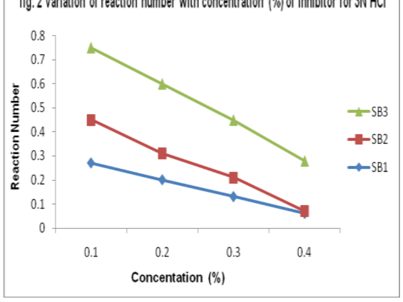


Table -3 shows the change in potential difference of the solutions with and without inhibitors. It can be observed from the table that initially there is a sharp rise in potential difference for all the solutions without and with inhibitors and then values becomes almost constant. It shows that initially the electrochemical reaction occurring in all the solutions is fast which becomes gradually slow due to adsorption of inhibitors on the metallic surface. The corresponding variation of potential with time in 2.5N HCl for 0.1% concentration of inhibitor for aluminium are shown in fig.3.

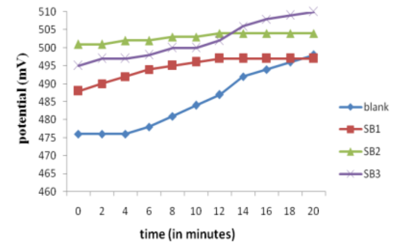


Fig 3: Variation of potential with time for aluminium in 2.5N HCl (0.1% concentration of inhibitors)

Conclusion

Results obtained by the present investigation revealed that all the three Schiff's bases act as effective corrosion inhibitor and the sequence of anticorrosive effectiveness is $SB_2 > SB_1 > SB_3$ and inhibition efficiency increases with increasing acid strength as well as that of inhibitor. Results revealed by both weight loss method and thermometric method are in good agreement with each other. Further, potential studies support the results and conclusions obtained by two said methods.

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Table-1

Weight loss ΔW inhibition efficiency (η%), and corrosion rate data for aluminium in HCl solutions with given inhibitor additions

Conc. of inhibitor	1N HCl (48 hours)			1.5 N HCl (5 hours 15min.)			2 N HCl (1 hou r 5min.)			2.5 N HCl (19 min.)		
(%)	Δw (mg)	Inhibition efficiency (η%)	Corrosion rate (mm/yr)	Δw (mg)	Inhibition efficiency (η%)	Corrosion rate (mm/yr)	Δw (mg)	Inhibition efficiency (η%)	Corrosion rate (mm/yr)	Δw (mg)	Inhibition efficiency (η%)	Corrosion rate (mm/yr)
uninhibited	261	-	47.63	260	-	433.82	277	-	2239.86	261	-	7220.08
SB_1												
0.1	111	57.47	20.25	105	59.61	175.20	69	75.09	557.94	25	90.42	691.57
0.2	85	67.43	15.51	68	73.84	113.46	50	81.94	404.30	20	92.33	553.26
0.3	69	73.56	12.59	53	79.61	88.43	42	84.83	339.61	15	94.25	414.94
0.4	55	78.92	10.03	40	84.61	66.74	36	87.00	291.10	10	96.16	276.63
SB_2												
0.1	80	69.34	14.60	74	71.53	123.47	46	83.39	371.96	12	95.40	331.95
0.2	72	72.41	13.14	64	75.38	106.78	38	86.28	307.27	8	96.93	221.30
0.3	60	77.01	10.95	42	83.38	70.08	32	88.44	258.75	4	98.46	110.65
0.4	40	84.67	07.3	25	90.38	41.71	21	92.05	169.80	2	99.23	55.32
SB_3												
0.1	200	23.27	36.50	190	26.92	317.02	97	64.98	784.35	38	85.44	1051.20
0.2	190	27.20	34.67	119	54.23	198.56	68	75.45	549.85	32	87.73	885.22
0.3	132	49.42	24.09	70	73.07	116.80	44	84.11	355.79	28	89.27	774.56
0.4	98	62.45	17.88	44	83.07	73.41	29	89.53	234.49	21	91.95	580.92

Table 2

Reaction Number (RN) and inhibition efficiency (η%) for aluminium in HCl solutions with given inhibitor addition Temperature : 303 ± 0.1 K

	1N HCl (48 hours)		2 N HCl (1 hour 5min.)		3 N HCl (10 min.)	
Concentration of inhibitor (%)	Reaction Number (K Min^{-1})	Inhibition efficiency (η)	Reaction Number (K Min^{-1})	Inhibition efficiency (η)	Reaction Number (K Min^{-1})	Inhibition efficiency (η)
uninhibited	0.00138	-	0.14615	-	1.45000	-
SB_1						
0.1	0.00097	29.71	0.06461	55.75	0.27000	81.37
0.2	0.00086	38.68	0.06153	57.90	0.20000	86.20
0.3	0.00072	47.82	0.04769	67.41	0.13000	91.03
0.4	0.00031	77.53	0.02923	80.01	0.06000	95.86
SB_2						
0.1	0.00093	32.60	0.04153	71.59	0.18000	87.58
0.2	0.00083	39.85	0.03846	73.71	0.11000	92.41
0.3	0.00045	67.39	0.02307	84.25	0.08000	94.48
0.4	0.00027	80.43	0.02153	85.28	0.01000	99.31
SB_3						
0.1	0.00100	27.23	0.06615	55.75	0.30	79.31
0.2	0.00900	34.78	0.06307	56.87	0.29	80.00
0.3	0.00079	42.75	0.05230	64.20	0.24	83.44
0.4	0.00064	53.62	0.04615	68.44	0.21	85.51

Table 3
Potential difference data for aluminium in 2.5M HCl solutions with and without inhibitor addition

		SB_1				SB_2				SB_3			
concentration	blank	0.1%	0.2%	0.3%	0.4%	0.1%	0.2%	0.3%	0.4%	0.1%	0.2%	0.3%	0.4%
Time(min.)	-	-	-	-	-	-	-	-	-	-	-	-	-
0	476	488	484	485	488	501	485	477	472	495	472	460	465
1	476	488	484	485	488	501	485	477	472	498	472	460	465
2	476	490	484	485	488	501	487	479	472	500	472	460	465
3	476	490	484	485	488	502	488	480	472	512	473	461	465
4	476	492	485	486	488	502	490	482	473	520	473	461	465
5	477	493	485	486	488	502	492	485	473	524	473	461	465
6	478	493	485	486	489	502	493	486	473	527	473	461	466
7	480	494	485	486	489	503	493	486	473	528	474	462	466
8	481	494	486	487	489	503	493	486	473	530	474	462	466
9	482	495	486	487	489	504	493	486	473	533	474	462	466
10	484	495	486	487	489	504	493	486	473	534	474	462	466
11	486	496	486	487	489	504	493	486	473	535	474	462	466
12	487	496	486	488	489	504	493	486	473	535	474	462	466
13	489	497	487	488	489	504	493	486	473	535	477	465	466
14	492	497	487	488	489	504	493	486	473	535	477	465	466
15	493	497	487	488	489	504	493	486	473	535	477	465	466
16	495	497	487	488	489	504	493	486	473	535	477	465	466
17	496	497	487	488	489	504	493	486	473	535	477	465	466
18	497	497	487	488	489	504	493	486	473	535	477	465	466
19	497	497	487	488	489	504	493	486	473	535	477	465	466