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Corrosion restriction and adsorption characteristics of Nitrogen–containing ligands on Aluminium in different concentrations of Hydrochloric acid

Suresh Sahu
Government Engineering College, Ajmer, Rajasthan, India
sureshsahu@ecajmer.ac.in

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Abstract

In the present paper, we are presenting mass loss to analyse the corrosion inhibition of aluminium in 0.5N HCl, 1.0N HCl, and 2.0N HCl solutions by three novel nitrogen-containing ligands (Schiff's bases) viz, N(vanillidine)-4-methyl-1-phenylimine (SB_1), N(vanillidine)-4-methoxy-1-phenylimine (SB_2), N(anisidine)-1-napthylimine (SB_3). The efficiencies have been compared with those of parent aldehyde and amines from which Schiff's base has been derived. Results of inhibition efficiencies observed from these two methods are in good agreement and have been found to depend on the concentrations of inhibitors as well as those of acids. The inhibitory efficacy of all inhibitors increases with increasing inhibitor concentration. Efficacy also increases with increasing concentration of acids. Adsorption of the inhibition molecule on the aluminium surface was consistent with the Langmuir isotherm.

Keywords: Mass loss technique, Aluminium, Corrosion inhibition.

Introduction

Aluminium and its alloys are widely utilised materials due to their significant technological value and extensive industrial applications. Aluminium has a face-centred cubic crystal structure, due to which it has resistance to brittle cleavage fracture at low temperatures. This enables aluminium to be used for making tanks and vessels to hold reactants and products at a very low temperature.

They are commonly found in sectors such as aerospace, household industries, and marine applications. However, despite their inherent corrosion resistance, aluminium and its alloys can still be susceptible to corrosion under certain conditions[1,2].

The reasons for the success of aluminium are clear. It has good corrosion resistance, which allows it to maintain an untarnished and attractive natural surface in the atmosphere with little on treatment. Due to low density, relative economy and excellent fabricating properties, it is widely used in every house[3,4].

In the case of aluminium being exposed to different concentrations of hydrochloric acid (HCl) solutions, such as in pickling, chemical etching, or electrochemical etching processes, corrosion inhibitors should be utilised. Hydrochloric acid can attack and dissolve the protective oxide film on aluminium, making it more vulnerable to corrosion. The solubility of the oxide film on aluminium increases at pH values below 4 and above 9. At these pH levels, the aluminium surface is more prone to uniform attack, where corrosion occurs evenly across the surface. The use of corrosion inhibitors in these situations is crucial to mitigate the corrosion process.

Many Schiff bases have been reported as effective corrosion inhibitors for different metals and alloys in the acidic media[5,6].

Generally, heterocyclic compounds containing heteroatoms nitrogen, oxygen and sulphur offer effective corrosion resistance by getting adsorbed on the metal surface through the lone pair of electrons present on these atoms[7-9]. This process may block the active site and hence decrease the corrosion rate. The efficiency of heterocyclic compounds depends upon the electron density of the heteroatom[10,11].

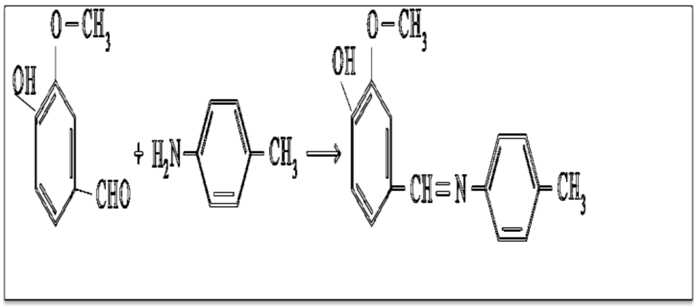
Schiff's bases act as corrosion inhibitors for aluminium. When the concentrations of the inhibitors were increased, the inhibition efficiencies increased with increasing surface coverage[12-14].

In the present study, three novel nitrogen-containing ligands (Schiff's bases) Viz N(vanillidine)-4-methyl-1-phenylimine (SB_1), N(vanillidine)-4-methoxy-1-phenylimine (SB_2), and N (anisidine)-1-napthylimine (SB_3), have been tested for their corrosion inhibitive properties for mild steel in various concentrations 0.5, 1.0, 2.0 N of hydrochloric acid by employing mass loss and thermometric methods.

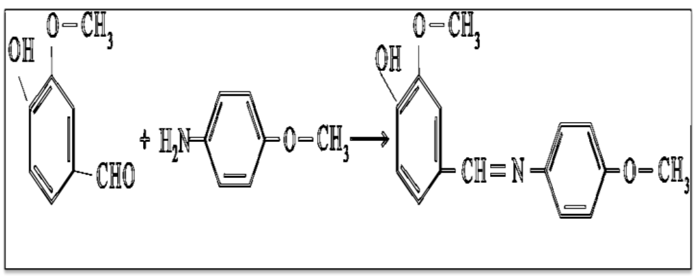
Materials and Methods

Rectangular specimens of Aluminium of dimensions 2.50x1.55x 0.02 cm with a small hole of about 2 mm diameter near the upper edge were used for the determination of mass loss measurement. Specimens were cleaned by buffing to produce a mirror finish with the help of emery paper and then degreased with acetone. Each specimen was suspended by a glass hook and immersed in a beaker containing 50 ml of test solution at room temperature, and left exposed to air evaporation. Duplicate experiments were performed in each case, and the mean value of mass losses was calculated.

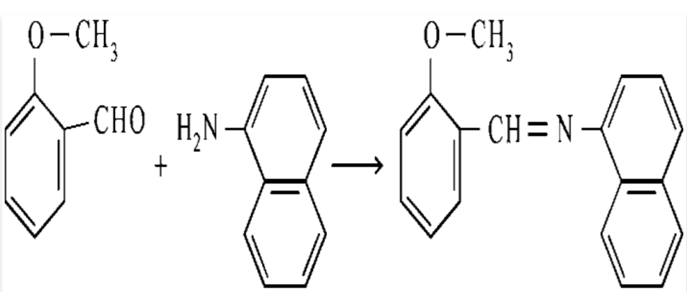
Preparation of Test Solution: The hydrochloric and sulphuric acids and a mixture of both acids of different concentrations were prepared using distilled water. The respective solutions of novel nitrogen-containing ligands (Schiff's bases) were prepared by taking respective quantities of compounds, and ethanol as solvents.



Scheme-1: Preparation of N (vanillidine)-4-methyl-1-phenylimine (SB_1) from vanillin and p-toluidine.



Scheme-2: Preparation of N (vanillidine)-4-methoxy-1-phenylimine (SB_2) from vanillin and p-anisidine.



Scheme-3: Preparation of N (anisidine)-1-napthylimine (SB_3) from anisaldehyde and α-napthylamine.

To observe the influence of various parameters like inhibitor concentrations, acid concentrations and time, the corrosion inhibition efficacy (η %) of the compounds has been calculated by mass loss method using the following equation:
Inhibition Efficacy (η %) = 100 ($\Delta M_u - \Delta M_i$) / ΔM_u

Where: ΔM_u is the mass loss in uninhibited solution, ΔM_i is the mass loss in inhibited solution.

The degree of surface coverage (θ) can be calculated as:
$\theta = (\Delta M_u - \Delta M_i) / \Delta M_u$
Where: ΔM_u is the mass loss in uninhibited solution, ΔM_i is the mass loss in inhibited solution.

The corrosion rate in mmpy (mm per year) was obtained by the following equation:
Corrosion rate= ΔM x 87.6 /A T D
Where: ΔM is expressed in mg. A is expressed in square cm, T is the time of exposure in hours. D is metal density in gcm^{-3}.

Results and Discussion

The percentage of inhibition efficiency and surface coverage obtained from weight loss method at different concentrate of inhibitor for the corrosion of Schiff base in 0.5N, 1.0N, 2.0N HCl for an immersion period of 24 hour (0.5N HCl), 4 hours (1.0N HCl), 2 hours (2.0N HCl) and 30 at 298+0.1K, area of exposure $7.7 cm^2$ are shown in Table-1, 2 and 3. The results show that inhibitor actually inhibited the corrosion of aluminium in 0.5N, 1.0N, 2.0N HCl at constant temperature (298+0.1K) the inhibition efficacy increases with increasing inhibitor concentration.

The results reveal that novel nitrogen-containing ligands effectively reduce the corrosion rate of Aluminium in acidic media by showing inhibition efficiency up to 93.61% and can be safely used without hydrogen damage, toxic effects and pollution.

Schiff's bases are more effective corrosion inhibitors than corresponding aldehydes and amines because they contain nitrogen and oxygen atoms, which are responsible for the adsorption, which may block the active sites of metals and hence decrease the corrosion rate.

Adsorption isotherm: Figure–1,2,3 shows Langmuir adsorption isotherm for the adsorption of N(vanillidine)-4-methyl-1-phenylimine (SB_1), N(vanillidine)-4-methoxy-1-phenylimine (SB_2), N(anisidine)-1-napthylimine (SB_3) on the Aluminum surface. The valves of adsorption parameters deduced from the isotherm are given in the Table-1, 2 and 3. From the results obtained, it is significant to note that these plots are linear with the slopes equal to the unity, indicating strong adherence of the adsorption data to the assumption underlying the Langmuir adsorption isotherm. As we can see from Figure-1,2,3 of N(vanillidine)-4-methyl-1-phenylimine (SB_1), N (vanillidine) -4-methoxy-1-phenylimine (SB_2), N(anisidine)-1-napthylimine (SB_3) inhibitor was found to obey the Langmuir adsorption isotherm.

Table-1: Corrosion data for different concentrations of novel nitrogen-containing ligands (Schiff's bases) for Aluminum in a 0.5N HCl at 298 ±0.1K. (lab experiment). Area of exposure – 7.75 cm^2. Time of exposure – 24 hrs.

SB	Inhibitor concentration (%)	Mass Loss ΔM (mg)	Inhibition efficacy (η %)	Corrosion rate (mmpy)	Surface coverage (θ)
SB_1	Blank	235	-	14.0976	-
	0.12	106	54.89	6.3589	0.5489
	0.24	82	65.10	4.9191	0.6510
	0.36	64	72.76	3.8393	0.7276
	0.48	32	86.38	1.9196	0.8638
	0.60	22	90.63	1.3197	0.9063
SB_2	Blank	235	-	14.0976	-
	0.12	104	55.74	6.2389	.5574
	0.24	80	65.95	4.7992	0.6595
	0.36	62	73.61	3.7193	0.7161
	0.48	46	76.17	3.3594	0.7617
	0.60	37	84.25	2.2196	0.8425
SB_3	Blank	235	-	14.0976	-
	0.12	96	59.74	5.7590	0.5914
	0.24	42	82.12	2.5195	0.8212
	0.36	21	91.06	1.2597	0.9106
	0.48	19	91..91	1.1398	0.9191
	0.60	15	93.61	0.8998	0.9361

Table–2: Corrosion data for different concentrations of novel nitrogen-containing ligands (Schiff's bases) for Aluminum in 1.0 N HCl at 298 ± 0.1K. (lab experiment). Area of exposure – 7.75 cm^2. Time of exposure – 4 hrs.

SB	Inhibitor concentration (%)	Mass Loss ΔM (mg)	Inhibition efficacy (η %)	Corrosion rate (mmpy)	Surface coverage (θ)
SB_1	Blank	33	-	11.8767	-
	0.12	17	48.48	6.1183	0.4848
	0.24	14	57.57	5.0386	0.5757
	0.36	11	66.66	3.9589	0.6666
	0.48	9	72.72	3.2391	0.7272
	0.60	7	78.78	2.5193	0.7878
SB_2	Blank	33	-	11.8767	-
	0.12	18	45.45	6.4782	0.4545
	0.24	15	54.54	5.3985	0.5454
	0.36	12	63.63	4.3188	0.6363
	0.48	6	81.81	2.1594	0.8181
	0.60	4	87.87	1.4396	0.8787
SB_3	Blank	33	-	11.8767	-
	0.12	16	51.51	5.7584	0.5151
	0.24	13	60.60	4.6787	0.6060
	0.36	8	75.75	2.8792	0.7575
	0.48	5	84.84	1.7995	0.8484
	0.60	3	90.90	1.0797	0.9090

Table–3: Corrosion data for different concentrations of novel nitrogen-containing ligands (Schiff's bases) for Aluminum in 2.0 N HCl at 298 ± 0.1 K. (lab experiment). Area of exposure – 7.75 cm^2. Time of exposure – 2 hrs.

SB	Inhibitor concentration (%)	Mass Loss ΔM(mg)	Inhibition efficacy (*η* %)	Corrosion rate (mmpy)	Surface coverage (*θ*)
SB_1	Blank	39	-	28.0761	-
	0.12	19	51.28	13.6781	0.5128
	0.24	17	58.41	12.2363	0.5641
	0.36	12	69.23	8.6388	0.6923
	0.48	9	76.92	6.4791	0.7692
	0.60	7	82.05	50393	0.8205
SB_2	Blank	39	-	28.0761	-
	0.12	18	53.84	12.9582	0.5384
	0.24	16	58.97	11.5184	0.5897
	0.36	14	64.10	10.0786	0.6410
	0.48	8	79.48	5.7592	0.7948
	0.60	6	84.61	4.3194	0.8461
SB_3	Blank	39	-	28.0761	-
	0.12	15	61.53	10.7985	0.6153
	0.24	13	66.66	9.3587	0.6666
	0.36	11	71.79	7.9184	0.7179
	0.48	10	74.35	7.1990	0.7435
	0.60	5	87.17	3.5995	0.8717

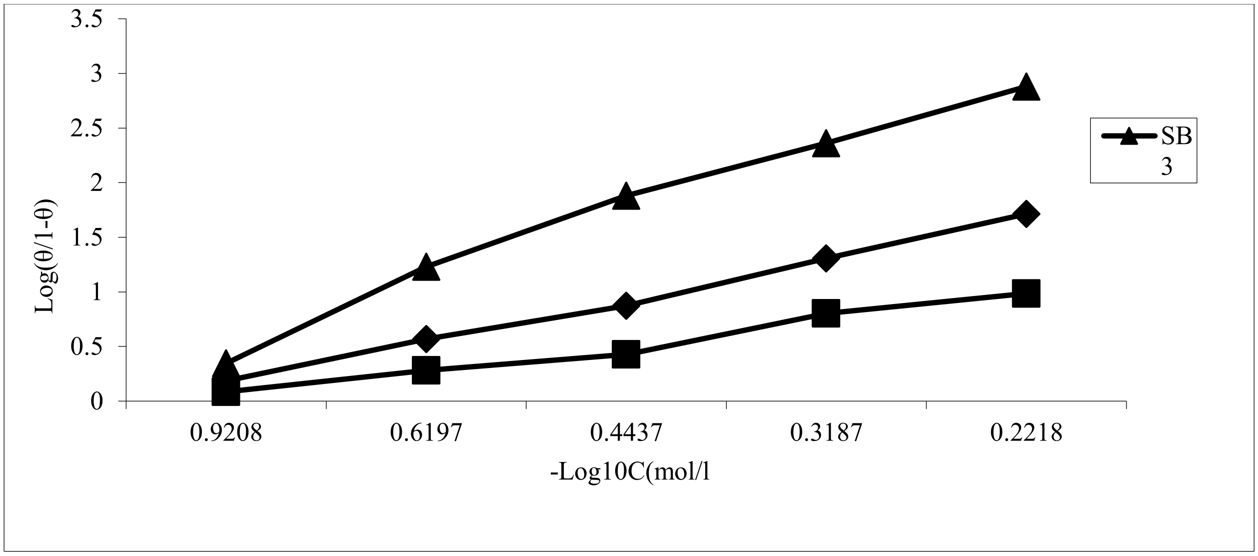


Figure-1: Langmuir adsorption isotherm for Aluminium in 0.5N hydrochloric acid containing Schiff's bases.

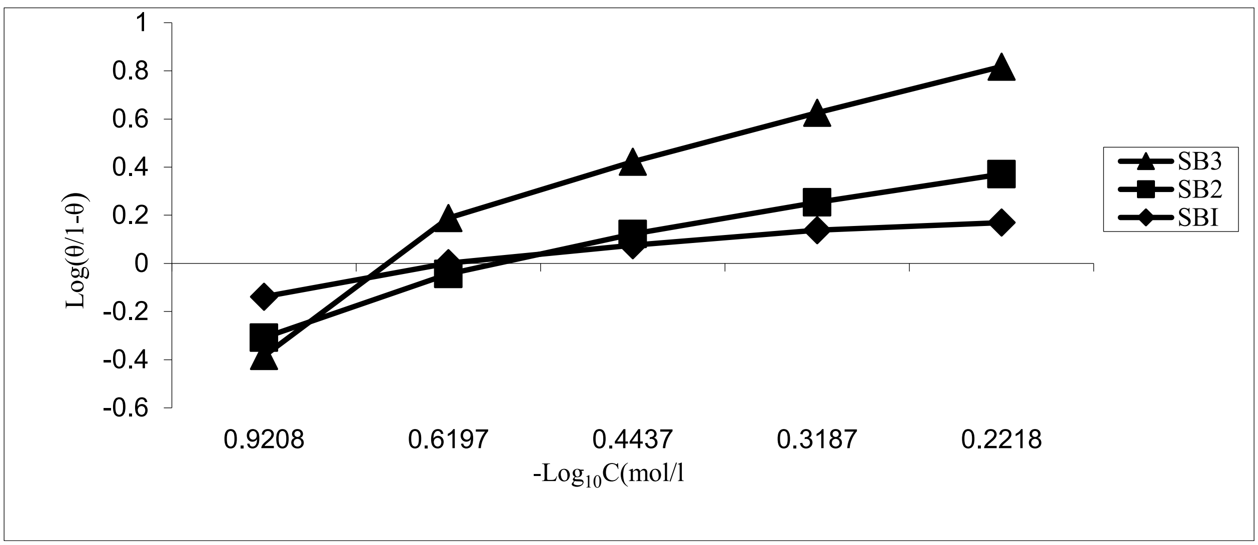


Figure-2: Langmuir adsorption isotherm for Aluminium in 1.0 N hydrochloric acid containing Schiff's bases.

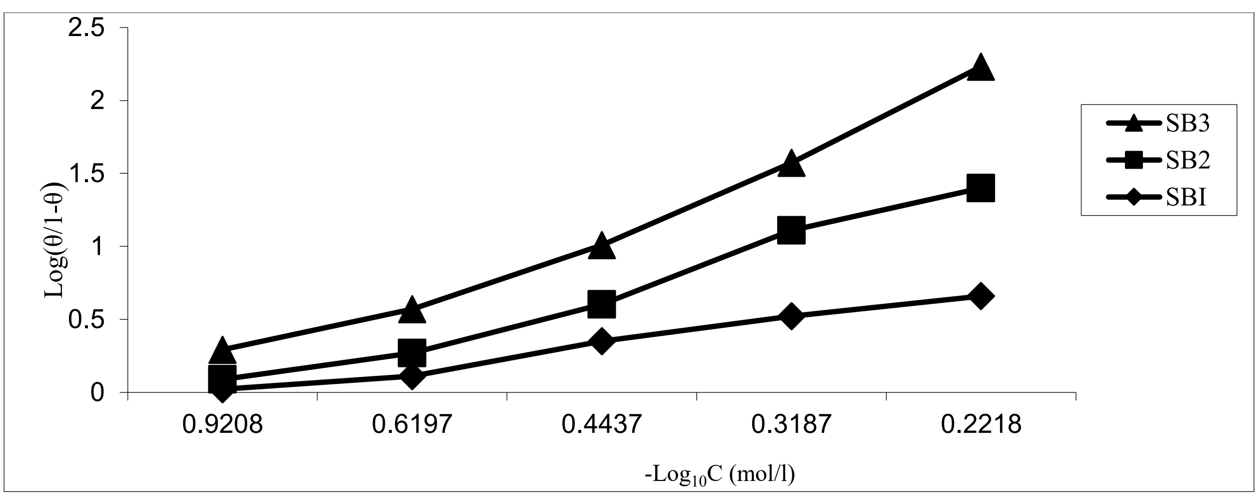


Figure-3: Langmuir adsorption isotherm for aluminium in 2.0 N hydrochloric acid containing Schiff's base.

Conclusion

The novel nitrogen-containing ligands showed promising results for corrosion inhibition of aluminium in the presence of different concentrations of HCl. The synthesized Schiff bases inhibits the corrosion of aluminium in different concentrations of HCl solutions with inhibition efficacy of 93.61% (0.5N HCl), 90.90% (1.0N HCl) and 87.17 (2.0N HCl), which are effective in reducing corrosion of the aluminium surface at temperature of 298+0.1K.

The adsorption of the inhibitor Schiff base was consistent with the Langmuir adsorption isotherm. The inhibitor molecule adsorbed on the aluminum metal surface and tend to retard the rate of corrosion by reducing the number of available sites for corrosion. From the mass loss data it is concluded that the Schiff's base effectively reduce the corrosion rate of Aluminium in different concentrations of HCl and can be safely used without hydrogen damage, toxic effect and pollution.

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