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SYNTHESIS, CHARACTERIZATIONS AND ANTI-CORROSION SCREENING OF SADIMINE AND BROSADIMINE

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Abstract

This paper deals with a review of the inhibition activity of a Schiff bases on the deterioration of mild steel in hydrochloric acid media. Two Schiff base ligands namely N,N'-Bis(salicylidene)-ethylenediamine (Sadimine) and N,N'-Bis(bromosalicylidene)-ethylenediamine (Brosadimine) were synthesized from the condensation reactions of salicylaldehyde or 5-bromosalicylaldehyde with ethylenediamine respectively and evaluated as corrosion inhibitor for mild steel in 1 M HCl solution using weight loss method. The use of inhibitors is one of the most practical methods for protection of mild steel against corrosion in acidic media. Schiff bases are widely being employed in such applications. This paper highlights the influence of structure–inhibition activity relationship of Schiff base compounds on their performance as corrosion inhibitors of mild steel in acid media. Sadimine and Brosadimine show appreciable corrosion inhibition efficiency against the corrosion of mild steel in 1 M HCl solution at room temperature. It has been found that Brosadimine shows greater corrosion inhibition efficiency than Sadimine due to extra halogen group presence in the structure. As the concentration of studied inhibitors increases, the corrosion inhibition efficiency of the prepared compounds also increases. This study demonstrated that corrosion inhibitors for metals and alloys can preserve the quality and life of metals from corrosion.

Keywords*: Schiff bases, corrosion inhibitor, weight loss method, mild steel*

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Introduction

A Schiff base also known as azomethine is a compound that consists of carbon-nitrogen double bond where the nitrogen are connected to an aryl or alkyl group but not hydrogen (Golcu *et al*., 2005). A Schiff base was prepared through condensation of primary amine with a carbonyl group namely aldehyde or ketone (Noordin *et al*., 2010). As stated by Hassan *et al*. (2015), Schiff base shows a promising result as inhibitors for corrosion of mild steel, aluminium, copper and zinc in acidic media.

Mild steel has been widely used in various industries such as engineering fabrications including bridge work, buildings, steam engine parts and automobiles, which are exposed to corrosive environments such as acid rain. These equipments need to be clean regularly because of the precipitation of oxides and carbonates due to the diminished heating transmission (Dadgarinezhad & Baghaei, 2010).Acid solutions such as hydrochloric acid and sulphuric acid are commonly used in order to remove undesirable scale and corrosion products from metals. However, these acids attack metal and prone to corrosion. The use of inhibitors is one of the most practical methods for protection of mild steel against corrosion in acidic media. The study of corrosion behaviour in corrosive media has continued to attract substantial attention because of many important applications of the metals. Organic

compounds containing heteroatoms including nitrogen, sulfur and/or oxygen with polar functional groups and conjugated double bonds have been reported as an effective corrosion inhibitor. The inhibiting action of these compounds usually due to their adsorption onto the metal surface forming a protective layer, thus prevent it from corrosion (Yadav *et al*., 2010).

The aim of this study is to synthesize, characterized and evaluate the effectiveness of a Schiff base ligands namely Sadimine and Brosadimine as a surface protector of the mild steel against corrosion.

Methods

Synthesis of 1 *N,N' Bis*(salicylidene) ethylenediamine (Sadimine)

A 30 ml methanolic solution of ethylenediamine (1.3356 ml, 20 mmol) was added to 30 ml methanolic solution of salicylaldehyde (4.2477 ml, 40 mmol). The pH of the methanolic solution of salicylaldehyde was adjusted between 5 to 6 by using 1.0 M HCl. This mixture then was heated while stirring under reflux in oil bath at 60 ºC for 5 hours. Then, this mixture was lefted to cool at room temperature and the yellow solid product formed was collected by filtration and recrystallized with cold methanol and weight. Figure 1 shows the structure of Sadimine.

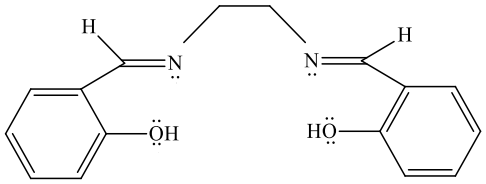

Figure 1 *N,N' Bis*(salicylidene) ethylenediamine (Sadimine)

Synthesis of *N,N'-Bis*(5-bromosalicylidene) ethylenediamine (Brosadimine)

A 15 ml methanolic solution of ethylenediamine (0.25 ml, 3.74 mmol) was added to 15 ml methanolic solution of 5-bromosalicylaldehyde (1.502 g, 7.47 mmol). The pH of methanolic solution of 5-bromosalicylaldehyde was adjusted between 5 to 6 by using 1.0 M HCl. This mixture then was heated under reflux in oil bath at 60ºC for 5 hours with continuously stirring. Then, this mixture was left to cool room temperature and the yellow solid product formed was collected by filtration and recrystallized with cold methanol. Figure 2 shows the structure of Brosadimine.

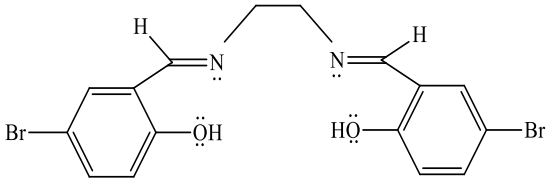

Figure 2 *N,N'-Bis*(5-bromosalicylidene) ethylenediamine (Brosadimine)

Characterization

Melting point was recorded in open capillaries using melting point apparatus model SMP10 stuart. Elemental analysis was performed on Flash EA110. The IR spectra of the ligands were recorded by using FT-IR spectrometer Spectrum 100 Perkin Elmer. UV-Visible spectroscopy was conducted by using T80+ PG Instrument.

Anti-corrosion screening

The anti-corrosion screening for the synthesized Sadimine and Brosadimine in 1.0 M HCl at room temperature was done by using weight loss measurement. The vial bottles were labelled 1 to 10 with each containing 1.0 M HCl solution. The first vial was labelled as a blank while the remaining vials contained the Schiff bases ligands as inhibitors with concentrations of 0.1 M, 0.01 M and 0.001 M, respectively. The mild steel coupons with 2 x 1.5 cm size was polished using emery paper, washed with distilled water and cleaned with acetone. The initial weight of the polished mild steel coupons were measured and recorded. After being weighed, the coupons were suspended in 10 ml of 1.0 M HCl in the absence or presence of different concentration of inhibitors and were allowed to stand at room temperature for 24 hours (Aouniti *et al*., 2015). After 24 hours, the mild steel coupons were removed, washed with distilled water, dried and reweighed again. All the tests were conducted in triplicate and average values were reported. The formula listed was used to calculate the Inhibition efficiency of the Sadimine and Brosadimine where W_o is the weight loss of mild steel coupons without inhibitor and W_i is the weight loss of mild steel coupons with inhibitor.

$$IE = \frac{Wo - Wi}{Wo}$$

$$\%IE = IE \times 100\ \%$$

Result and Discussions

The Schiff base ligands were formed by condensation reaction between ethylenediamine with salicylaldehyde or 5-bromosalicylaldehyde to obtain Sadimine ($C_{16}H_{16}N_2O_2$) and Brosadimine ($C_{16}H_{14}Br_2N_2O_2$).

Elemental Analysis

The elemental analysis of Sadimin and Brosadimine was found to have a good agreement with the calculated ones. Table 1 recorded the data for elemental analysis.

Table 1 Physical properties data for Sadimine and Brosadimine.

Schiff base	Molar mass (g/mol)	Colour	Yield (%)	Melting Point (^OC)	Elemental analysis Found (Calculated) (%)		
					C	H	N
Sadimine	268.31	Chrome Yellow	91.37	128	71.44 (71.56)	6.07 (5.96)	12.42 (10.43)
Brosadimine	426.10	Yellow	92.81	201	44.65 (45.06)	3.25 (3.29)	8.44 (6.57)

Infrared Spectroscopy

For Sadimine, a sharp band were observed at 1632.66 cm^{-1} assigned for v(*C=N*) stretching frequency of the azomethine group which indicates the successful formation of Schiff base

ligand. The appearance of band at 1497.26 cm^{-1} corresponding to *C=C* stretching frequency for benzene ring. Another two peaks that appeared in the spectrum are 1282.87 cm^{-1} and 1150.24 cm^{-1} are assignable to v(*C-O*) and *v*(*C-N*), respectively. For Brosadimine, the stretching band can be seen at 1632.91 cm^{-1} assignable to azomethine v(*C=N*) stretching mode. The peaks at range 1474.33 cm^{-1} were assigned to v(*C=C*) for aromatic ring. Other peaks observed in the spectrum at 1275.53 cm^{-1} and 1185.24cm^{-1} were assigned to v(*C-O*) and v(*C-N*). In contrast to Sadimine, the presence of bromine in the Brosadimine ligand was detected at region 1033.52 cm^{-1}. According to Pavia *et al*. (2015), aryl bromides absorbs between 1030 cm^{-1} and 1075 cm^{-1}. The IR data for the synthesized ligands were tabulated in Table 2 and Figure 3(a) and 3(b) shows the IR spectra of Sadimine and Brosadimine, respectively.

Table 2 Infrared data for the synthesized ligands, Sadimine and Brosadimine.

Ligands	Frequency				
	v(C=C)	v(C=N)	v(C-O)	v(C-N)	v(Aryl-Br)
Sadimine	1497.26	1632.66	1282.87	1150.24	-
Brosadimine	1474.21	1632.97	1275.40	1185.26	1033.52

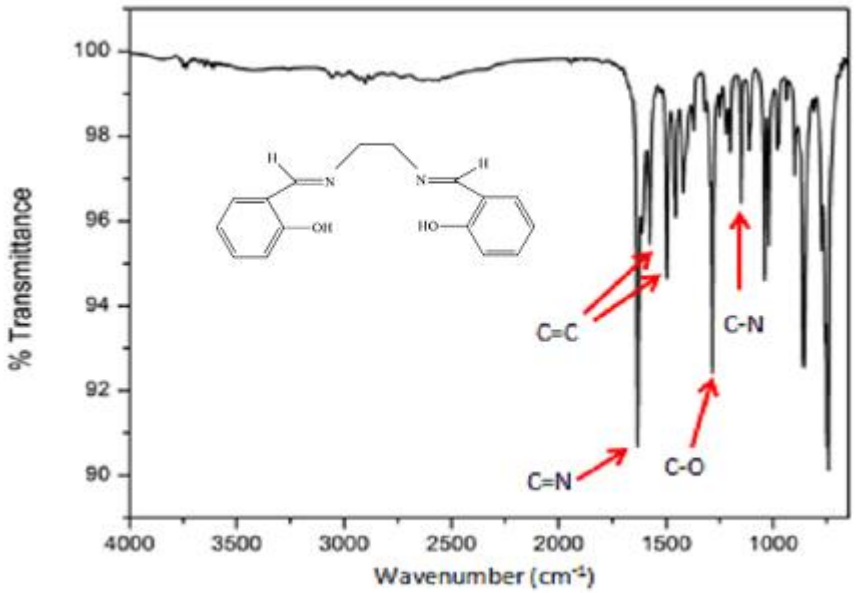

Figure 3(a) Infrared spectrum of Sadimine

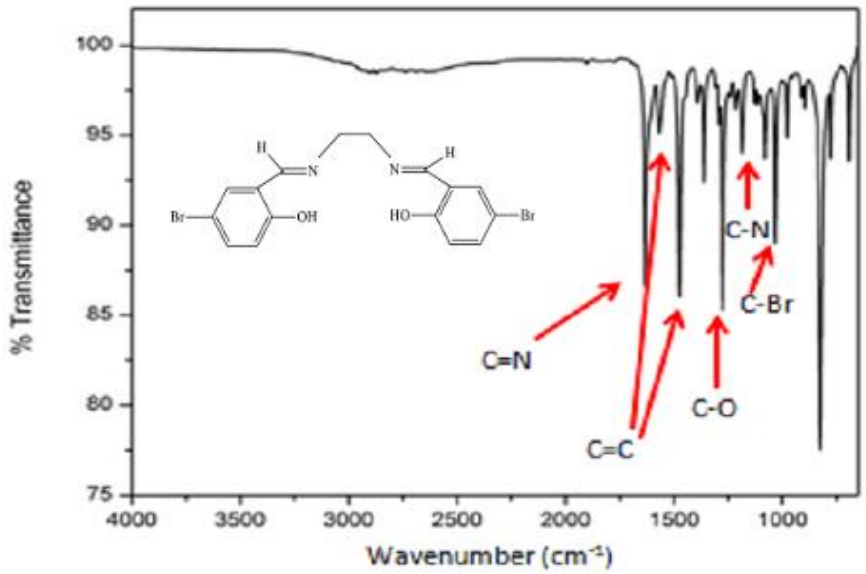

Figure 3(b) Infrared spectrum of Brosadimine

Ultraviolet-Visible spectroscopy

In this study, the UV spectra for both ligands, Sadimine and Brosadimine were obtained by using methanol as a blank and solvent in range of 200-400 nm and the result obtained was recorded in Table 3.

The UV-Vis absorption spectra of ligand comprised three absorption band maxima. For both Sadimine and Brosadimine the spectral data shows band at 215 and 221 nm which can be assigned to n-σ* transition. This transition is due to the presence of the nitrogen atom in the ligands which has one lone pair of electrons. In addition, the absorption band wavelength of 251 nm and 255 nm observed for both ligands were designated for π-π* transition due to the excitation of the π electron of aromatic system (Issa et al, 2005). While, band at 317 nm and 328 nm was attributed to the n-π*, can be related with C=N chromophore. According to Aranha et al. (2006), the band of C=N chromophore usually occurs at range between 270 and 400 nm. Figure 4 shows the UV-Vis spectrum of Sadimine and Brosadimine.

Table 3 UV-Vis data for Sadimine and Brosadimine.

Schiff base	Λ max (nm)	Molar absorptivity (ε)	Assign to
Sadimine	215	13300	n-σ*
	255	70500	π-π*
	317	24200	n-π*
Brosadimine	221	131200	n-σ*
	251	53900	π-π*
	328	17500	n-π*

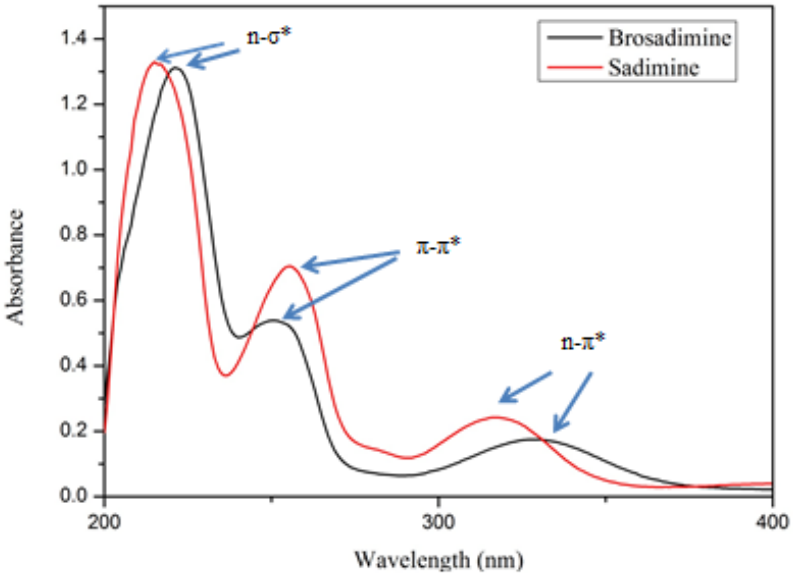

Figure 3 UV-Vis spectrum of Sadimine and Brosadimine.

Anti-corrosion screening

Table 4 Anti-corrosion screening of mild steel and inhibition efficiency.

Inhibitor	Inhibitor Concentration (M)	Mass loss (g)	IE	IE (%)	IE_{MS} (%)
Blank	-	0.0634	-	-	-
Sadimine	0.1	0.0222	0.6498	64.98	35.02
	0.01	0.0481	0.2413	24.13	75.91
	0.001	0.0568	0.1041	10.41	89.59
Brosadimine	0.1	0.0079	0.8754	87.54	12.46
	0.01	0.0342	0.4606	46.06	53.94
	0.001	0.0493	0.2224	22.24	77.76

Based on Table 4, it was clearly seen the inhibition efficiency increases with increasing inhibitor concentration for both Sadimine and Brosadimine. As stated by Asshashi *et al*. (2005), the inhibitor molecules were chemically adsorbed on the steel surface and cover some sites of the electrode surfaces. The inhibitors also form a complex with iron atom on the steel surface by forming a monomolecular layer which protects the steel from corrosion due to the presence of π electrons of the benzene ring and *C=N* which interact with steel surface (Chitra *et al*., 2010). In addition, they also mentioned that the interaction of lone pair of heteroatoms in the molecule with the steel surface may also be one of the factors to inhibit corrosion. When comparing both ligands, Brosadimine shows higher efficiency percentage for concentration of 0.1 M, 0.01 M and 0.001 M as compared to Sadimine. Similar findings were found by Şafak *et al*., (2012) where *Br* substituted Schiff base has more protective ability unsubstituted ligand. This may due to the substitution of heteroatom group (bromine) on the benzene which increase the electron density on the nitrogen of *C=N* group thus provide better adsorptivity to the mild steel (Asshashi *et al*., 2005). According to Hariharaputhran *et al.* as stated by Chitra *et al*. (2010), the inhibitive power, in general increases as the number of substituents on the benzene ring increases. Brosadimine has higher inhibitor efficiency due to their high molecular weight compared to Sadimine. So widely spread film was formed to protect the metal from contact with the acid in the corrosive environment. From the study done by Shetty (2019), larger molecule behaves as a good inhibitor for corrosion in line with

the finding in this study where Brosadimine shows higher inhibitor efficiency compared to Sadimine due to its high molecular weight compared to Sadimine. This factor makes Brosadimine can easily produce a film on the surface of mild steel thus inhibit corrosion. Therefore, the order of inhibitors efficiency is Brosadimine > Sadimine.

Conclusion

In conclusion, Sadimine and Brosadimine derived from aldehyde and amine were successfuly synthesized and characterized. This can be proven by the disappearance of *C=O* stretching frequency which were replaced with *C=N* bond.

For UV-Vis analysis, three important peaks were detected which are π-π*, n-σ* and n-π*. The π-π* showed the presence of benzene in the Schiff bases ligand. While, for n-σ* indicates the presence of the nitrogen atom in the ligands which has lone pair of electrons. The presence of *C=N* chromophore can be proved in the analysis as n-π* transition.

For anti-corrosion screening, it can be concluded that the inhibition efficiency increases with increase in inhibitor concentration for both Sadimine and Brosadimine. This may due to the presence of π electron of the benzene and lone pair of electrons on *N* atom from *CH=N* group. When comparing both ligands, the Brosadimine acts as a good inhibitor than Sadimine for mild steel. This may be due to the substituents of heteroatom (bromine) on the benzene which increase the electron density on the nitrogen of *C=N* group, thus provide better adsorptivity of the inhibitor on mild steel surface. In addition, the larger size of Brosadimine also play an important role in anti-corrosion screening where widely spread film formed on the surface of mild steel to protect the metal from contact with the acid in the corrosive environment, thus inhibit corrosion process.

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