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N-SALICYLIDENE-4-CHLOROANILINE AS PROTECTOR MATERIAL IN PREVENTING CORROSION PHENOMENON IN ACIDIC MEDIUM

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Abstract

Corrosion inhibitor was used for protection of metals and alloys in dealing with corrosion problems. Recently, Schiff base ligands have been reported as effective corrosion inhibitors due to the presence of Nitrogen, Sulphur, Oxygen, C=N group, and π-bond that can form a covalent bond and help in reducing corrosion rate. This research introduces N-salicylidene-4-chloroaniline as a protector material in preventing corrosion phenomenon (corrosion inhibitor) in our surrounding. The structure of this compound was characterised using CHN elemental analysis, FTIR, ^{1}HNMR, and UV-Vis spectroscopy. The combination results proved that this compound has C=N group and π-bond, which are good inhibitor properties. The corrosion inhibitor study in 1 M HCl solution was conducted via weight loss method. Results showed that the increase of inhibitor concentration will increase the inhibition efficiency and vice versa to immersion time, where the inhibition efficiency decreases with a longer exposure of mild steel in acidic medium. The conducted experiment shows that the percentage of inhibition efficiency is 80.0% in 78 hours reaction. It showed that the ligand can act as a good corrosion inhibitor in 0.1 M concentration, which slows the corrosion rate on the metal surface.

Keywords: *Acidic medium, corrosion inhibitor, mild steel, Schiff base.*

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1. Introduction

Schiff bases ligand derived from aromatic amines and aldehydes is not only easily prepared and cheaper material but also has a wide variety of applications including biological activities, catalyst, dyes, and corrosion inhibitor. Schiff bases ligand was recently reported as an effective corrosion inhibitor for mild steel, aluminium, copper, and zinc in acidic media (Duran et al., 2012). Schiff bases named after Hugo Schiff is derived from any of primary amino group reacted with an aldehyde or a ketone under a specific condition (da Silva et al., 2011). The separation of product or removal of water by acid catalysed dehydration reaction results in the formation of imine group (Mishra et al., 2013). The presence of the –C=N group in the Schiff base compound showed the inhibitive properties (Asegbeloyin et al., 2015). Corrosion is a serious problem that can lead to consequences including loss of mechanical strength and structural failure (Ashworth et al., 2013). It reduces the appearances of the building due to deterioration and can cause hazard or injury to the people from the structural failure (Jackson & Finsgar, 2014). This study is focusing on the synthesis and characterisation of Schiff base ligand in the presence of effective corrosion inhibitor group. Hence, the effectiveness of the synthesised ligand as a corrosion inhibitor in the acidic medium will be explored.

2. Materials and Methods

Preparation of N-salicylidene-4-chloroaniline

The synthesis route of *N*-salicylidene-4-chloroaniline is shown in Figure 1. The reaction started when 4-chloroaniline (1.2757 g, 0.01 mol) was dissolved in a 30 mL of absolute ethanol and added to a salicylaldehyde (1.2212 g, 0.01 mol) in a round bottom flask equipped with magnetic stirrer, condenser, and thermometer. The reaction mixture was refluxed at 80 °C for 5 hours with stirring. The product was cooled to room temperature and poured into a beaker containing ice-cooled water to precipitate the product. The precipitation was filtered using a piece of filter paper. The dried solid product that was recrystallized from ethanol and dried over anhydrous $CaCl_2$ in a desiccator gave a bright yellow powder (yield 72%; mp 106 °C). The product obtained was characterised using CHN analyser, UV-Vis, FTIR, and ^1H NMR spectroscopy.

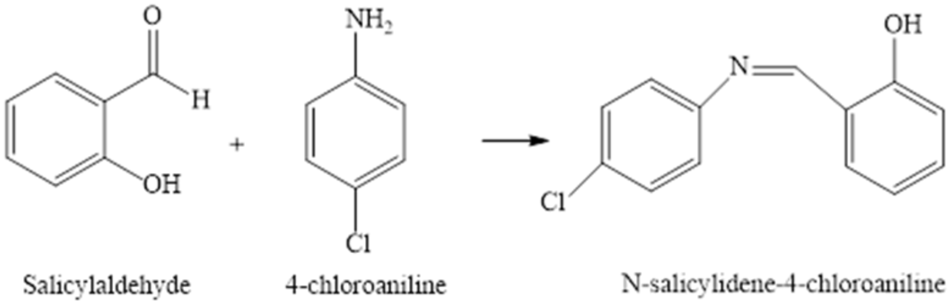

Figure 1. Synthesis route in preparation of *N*-salicylidene-4-chloroaniline (Xavier and Srividhya, 2014).

Weight loss measurement

The solution of 1 M hydrochloric acid was prepared by dilution of reagent grade of 37% HCl with distilled water in 250 mL volumetric flask and used as stock solution. The weight loss of mild steel specimen of size 2×1.5 cm in 1 M HCl without and with the addition of different concentrations of *N*-salicylidene-4-chloroaniline inhibitor was studied. The concentration of inhibitor was varied (0.1 M, 0.01 M, and 0.001 M) with time range between 6 to 78 hours. The changes in weight before and after immersion in acid solution were used to calculate the corrosion rate as expressed in g cm^{-2} h^{-1}. The corrosion rate, C_{RW} and the values of inhibition efficiency η_w (%) were calculated using Equations (1) and (2), respectively.

$$C_{RW} = \Delta W / S \times t \qquad (1)$$

$$\eta_w (\%) = [(C^o_{RW} - C_{RW}) / C^o_{RW}] \times 100 \qquad (2)$$

3. Results and Discussion

Characterisation of N-salicylidene-4-chloroaniline

The CHN elemental analysis indicates the successful formation of *N*-salicylidene-4-chloroaniline. The result obtained was in reasonable agreement in which the element presence was almost similar with the calculated values. The data are summarised in Table 1.

Table 1. Data of elemental analysis for N-salicylidene-4-chloroaniline

Schiff bases	**Colour**	**Percentage yield (%)**	**Melting point (ºC)**	**Elemental analysis found (calculated) (%)**		
				C	**H**	**N**
BL3	Bright yellow	72.08	106	67.28 (67.39)	4.27 (4.32)	5.69 (6.05)

The UV-Vis spectrum of *N*-salicylidene-4-chloroaniline inhibitor was measured in the range of 200-600 nm at room temperature. Based on Figure 2, the absorption peak for UV-Vis observed at 280 nm indicated the π-π* transition in benzene ring (Pavia et al., 2015) and the band at 380 nm were assigned due to n-π* transition associated with the azomethine chromophore (-C=N) (Usharani et al., 2012).

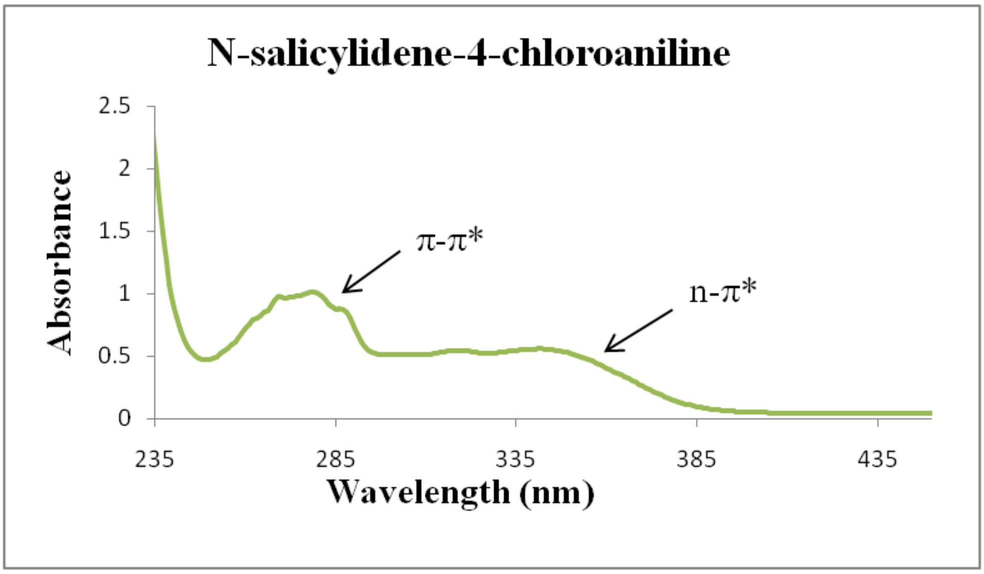

Figure 2. UV-ViS spectrum of *N*-salicylidene-4-chloroaniline

The FTIR spectrum in Figure 3 provides valuable information, which reveals the types of functional groups present in a molecule. The *N*-salicylidene-4-chloroaniline inhibitor showed the absorption peak at around 3400-3200 cm^{-1} due to a phenolic hydroxyl group in ligands. The stretching band appeared at 1630-1610 cm^{-1} assigned to azomethine (HC=N) linkage showed the successful reaction between amino and aldehydes moieties of the starting materials. The stretching band found at 1272 cm^{-1} region was assigned for C-O vibration. The strong band at 757 cm^{-1} was assigned as C-Cl bond.

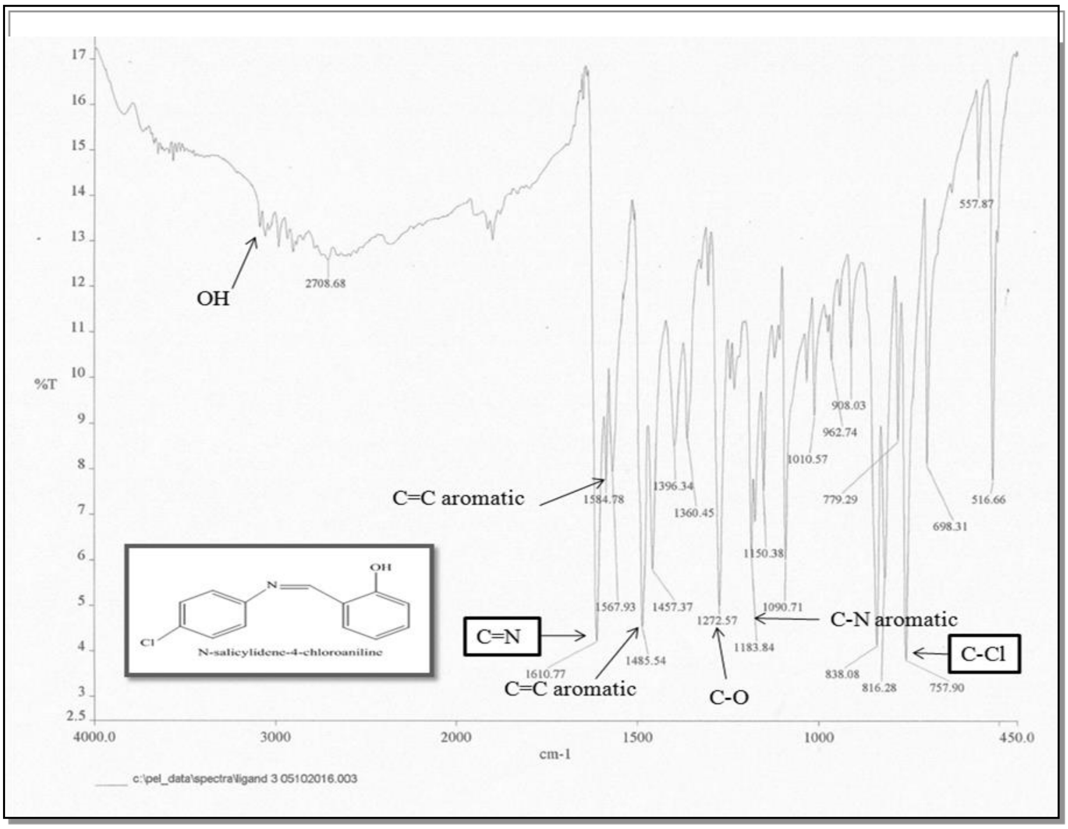

Figure 3: The FTIR spectrum for *N*-salicylidene-4-chloroaniline

Figure 4 shows that ^{1}H NMR spectrum of *N*-salicylidene-4-chloroaniline inhibitor exhibits multiplets in the range 6.9-7.96 ppm due to aromatic protons. It also shows a singlet at 8.73 and 13.05 ppm indicating the imine and aromatic phenol proton, respectively. The proton observed was shifted to the downfield of the spectrum due to the presence of electronegative atom (Pavia et al., 2015).

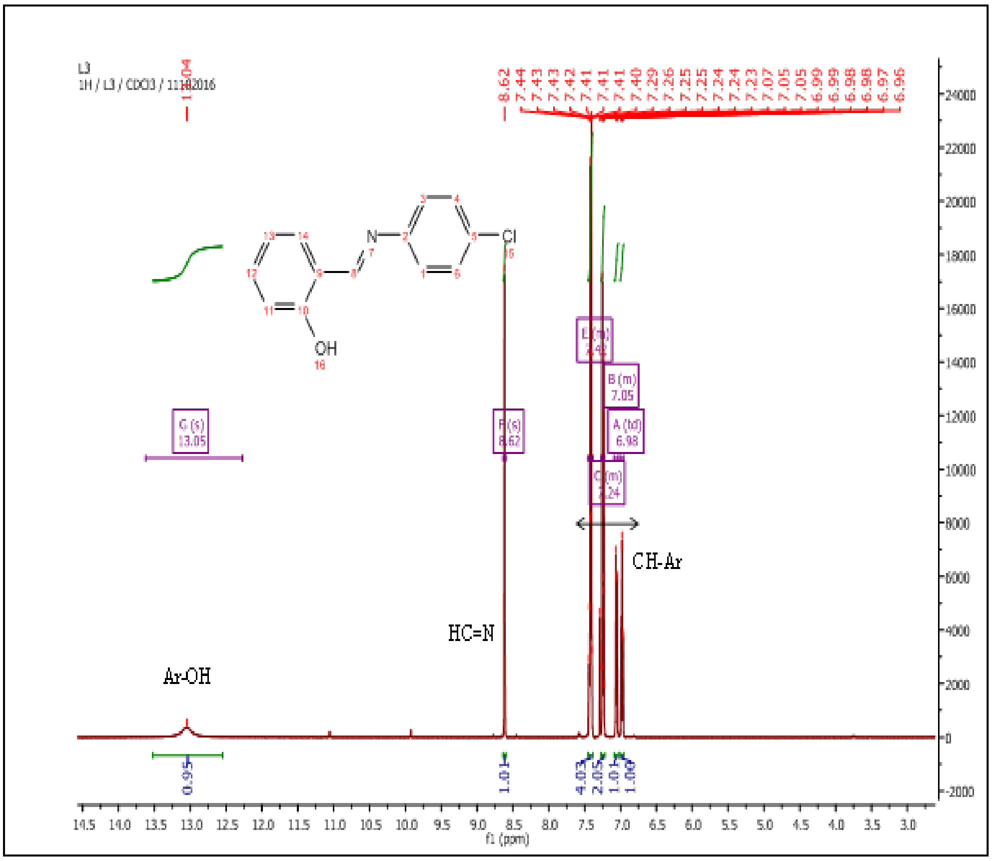

Figure 4. ^{1}H NMR spectrum of *N*-salicylidene-4-chloroaniline

Regarding the results obtained from the characterisation methods, including CHN elemental analysis, UV-Vis, FTIR, and ^{1}H NMR spectroscopy, the structure of *N*- salicylidene-4-chloroaniline inhibitor can be confirmed as illustrated in Figure 1.

Corrosion Inhibition Study: Effect of corrosion inhibitor concentration

The synthesis of *N*-salicylidene-4-chloroaniline was applied as corrosion inhibitors of mild steel coupon in 1 M HCl solution. The inhibition efficiencies were observed to increase with the raising inhibitor concentration (Duran et al., 2002). Based on Table 2, 0.1 M inhibitor concentration shows the most inhibition efficiency for the *N*-salicylidene-4-chloroaniline inhibitor followed by 0.01 M and 0.001 M inhibitor concentrations. This is due to the larger coverage of tested mild steel coupon with inhibitor molecules. The inhibitor molecules take an important role to protect the mild steel surface by the chemical adsorption on steel surface (Mainier et al., 2014). This process forms a monomolecular layer on the mild steel surface which inhibits the mild steel from corroding (Ashassi-sorkhabi et al., 2005).

Table 2. Data for corrosion inhibition efficiency of mild steel in 1 M HCl in absence and presence of *N*-salicylidene-4-chloroaniline inhibitor for 12 hours immersion time.

Inhibitor	**Concentration (M)**	**Weight loss, (ΔW)**	**Corrosion rate, (C_{RW})**	**Inhibition efficiency, (η_w,%)**
absence	0.0	0.0437	0.00121	-
presence	0.1	0.002	0.0000556	95.4
	0.01	0.0244	0.000678	44.0
	0.001	0.0309	0.000858	29.1

In addition, the presence of an electronegative group (chlorine) in the structure of *N*-salicylidene-4-chloroaniline also increased the inhibition properties. The electron pairs from chlorine may flow into the aromatic ring by π conjugation (resonance). The donor-acceptor interactions between free electron pairs of chlorine and π electron through chemisorptions form a protective thin film which protects the steel surface from corrosion (Vinutha & Venkatesha, 2016). The presence of benzene ring leads to high inhibition efficiency and increases the electron density on the nitrogen of the C=N group which can form a strong π bond. This occurs when HOMO electron in electronegative chlorine donates its electron towards unoccupied orbitals (LUMO) of iron steel (Ashassi-sorkhabi et al., 2005). The *N*-salicylidene-4-chloroaniline acts as an inhibitor when a bond forms by sharing electron between nitrogen and oxygen atom or π electron of the aromatic system with the mild steel surface (Andreani et al., 2015).

Corrosion Inhibition Study: Effect of immersion time

The efficiency of *N*-salicylidene-4-chloroaniline as an inhibitor was tested in duration immersion time between 6-78 hours. The results are illustrated in Figure 5. It can be observed that the percentage inhibition efficiency increased from 94.0% to 97.6% in the first 18 hours. This was due to the increase in adsorption of the protective film towards the metal surface. The inhibitor molecules were chemically absorbed on the steel surface and covered some sites of the steel surface (Al-Shafey et al., 2014). However, after 18 hours of immersion time, the inhibition efficiency started to decrease. The efficiency was reduced from 95.4% to 80.0% due to the increase in desorption of protective film on the metal surface. This effective layer that covered the steel from corrosion slowly became inefficient to protect the steel because of the depletion of available inhibitor molecules in the solution due to chelate formation between iron and *N*-salicylidene-4-chloroaniline inhibitor (Gupta & Quraishi, 2010). This effective layer still inhibited the corrosion rate up to 80.0% but its efficiency started to decrease due to long immersion time in the acidic medium. Thus, the *N*-salicylidene-4-chloroaniline inhibitor is protective as it can inhibit the corrosion rate up to 97.6%.

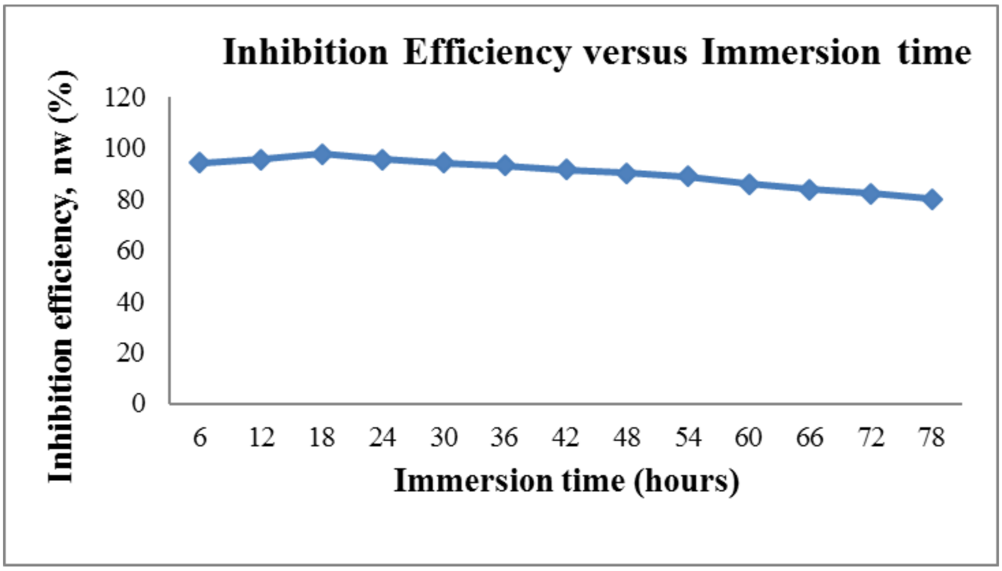

Figure 5. Graph for corrosion inhibition efficiency for mild steel in 0.1 M inhibitor concentration within 78 hours.

4. Conclusion

N-salicylidene-4-chloroaniline was successfully synthesised and applied as protector material in preventing corrosion phenomenon (corrosion inhibitor) in acidic medium. The synthesised compound at a concentration of 0.1 M showed good inhibition properties in a high concentration of acidic medium event at long immersion time (80.0% inhibition efficiency).

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