



Corrosion Inhibition of Azomethines Containing Hydroxyl Group at *Ortho* and *Para* Positions on Mild Steel

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ABSTRACT

The syntheses of salicylideneaniline (L1a) and 4-hydroxybenzaldehyde (L1b) was carried out via condensation reaction giving yields of 80.74% and 81.65% respectively. The compounds were characterised by physical and spectroscopic techniques, namely melting point, micro elemental analysis (C, H and N), ¹H Nuclear Magnetic Resonance (NMR) and Infrared (IR) spectroscopy. The characteristic $\nu(\text{C}=\text{N})$ peaks were observed at 1615 cm^{-1} and 1575 cm^{-1} respectively. Chronoamperometry (CA) was employed to electrodeposit both compounds on mild steel at 0.1 M inhibitor concentration in 0.3 M NaOH at three different potentials, +0.8 V, +1.05 V and +1.7 V. Formation of yellow imine films was observed on the mild steel. The corrosion behaviour of coated and uncoated mild steel was studied using Linear Polarization Resistance (LPR) in 0.5 M NaCl. Coated mild steel showed better corrosion resistance and with the highest inhibition efficiency of 90.34%, L1a provides a better protection against corrosion for mild steel than L1b.

Keywords: Azomethine, chronoamperometry, corrosion inhibition, electrodeposition, LPR

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INTRODUCTION

The use of mild steel is ubiquitous in everyday life in most constructions, vehicles, pipelines and even in household items. However, mild steel has its own disadvantages in which it has poor corrosion resistance. When iron or steel is exposed to atmospheric oxygen in the presence of water, the process of rusting takes place. Iron is degraded to ferric rust, a red-brown compound, which signals the electrochemical oxidation of the metal.

Inhibitors are chemicals when added in small amount into a system can protect it from corrosion. The inhibitors retard corrosion by either increasing the anodic or cathodic polarisation resistance of the cell or preventing the diffusion of ions onto the metallic surface (Harun, 2010). Many organic compounds have been studied for their corrosion inhibition potential, for example, the effect of organic nitrogenous compounds on the corrosion behaviour of iron and steel in acidic medium (Abdul Ghani et al., 2014) and these organic compounds are usually employed because of their rapid action (Myint et al., 1996; Behpour et al., 2009).

Azomethines or Schiff bases are commonly synthesised through condensation of primary amines with active carbonyl compounds and they were first reported in 1864 by Hugo Schiff (Cimerman et al., 2000). Schiff bases with their characteristic C=N functional group are known as nitrogen bearer inhibitors, commonly chosen due to the presence of lone pairs of electrons in their molecular structures. Their planarity increases the absorptivity on the active sites of metal surface as reported by several investigators (Hashim et al., 2014; Mallaiya et al., 2011; Ju et al., 2008). Electronic tuning of the molecular structures to study their adsorption behaviour, hence corrosion inhibition, may include addition of electron rich aromatic rings as well as electron donating and withdrawing moieties as reported by Sauri et al. (2009).

The purpose of this study was to synthesise and characterise two Schiff bases, salicylideneaniline (L1a) and 4-hydroxybenzaldehyde aniline (L1b) which have very similar chemical structures except for the position of –OH (Figure 1). The corrosion behaviour of mild steel coated with L1a and L1b was studied in 0.5 M NaCl using linear polarisation resistance (LPR) and compared with that of the uncoated mild steel. The differences of inhibition efficiency of the compounds are explained based on their chemical structures.

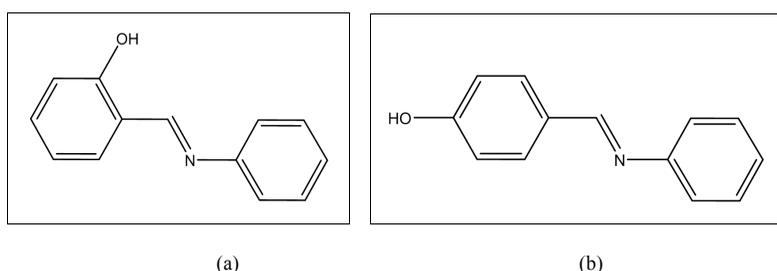


Figure 1. Molecular structures of (a) salicylideneaniline (L1a) and (b) 4-hydroxybenzaldehyde aniline (L1b)

METHOD

Materials

All the chemicals and solvents used were of analytical grade. Salicylaldehyde, 4-hydroxybenzaldehyde, aniline, absolute ethanol, chloroform, deuterated chloroform (CDCl_3) and deuterated dimethylsulfoxide (DMSO), and potassium bromide (KBr) were purchased from commercial suppliers and used without further purification. The micro-analytical data (C, H and N) of L1a and L1b were obtained from Thermo Scientific Flash 2000 Elemental Analyzer. Melting points were determined using Stuart SMP10. Perkin-Elmer model 1750X

FTIR spectrophotometer using KBr pellets was employed to record Infrared (IR) spectra of synthesised compounds in range of 4000-450 cm^{-1} . ^1H NMR spectra were analysed on a Bruker Varian-500 and 600 MHz spectrometer using deuterated chloroform (CDCl_3) and deuterated dimethylsulfoxide (DMSO) and expressed in a unit of parts per million (d, ppm).

Synthesis and Characterisation Of Salicylideneaniline (L1a)

A mixture of 20 mmol of salicylaldehyde and 20 mmol of aniline in absolute ethanol (15 mL) was refluxed for three hours. The yellow precipitate formed was filtered off and washed thoroughly with cold ethanol, dried and weighed (3.185 g, 80.74%). Melting point 53°C , (Found: C, 78.16; H, 5.57; N, 6.95. $\text{C}_{13}\text{H}_{11}\text{NO}$ requires C, 79.16; H, 5.62; N, 7.10 %); n_{max} (KBr): C=N, 1615; Ar-OH, 1274; C=C, 1400 cm^{-1} ; ^1H NMR (CDCl_3) δ/ppm : 7.24-7.31 (4 H, m, aromatic), 7.35-7.45 (4H, m, aromatic), 8.63 (1 H, s, CH), 13.27 (1H, s, OH).

Synthesis and Characterization of 4-hydroxybenzalaniline (L1b)

A mixture of 20 mmol of 4-hydroxybenzaldehyde and 20 mmol of aniline in absolute ethanol (15 mL) was refluxed for 3 hours. The light yellow precipitate formed was filtered off and washed thoroughly with cold ethanol. It was air dried and weighed (3.2208 g, 81.65%). Melting point 198°C , (Found: C, 78.15; H, 5.58; N, 6.90. $\text{C}_{13}\text{H}_{11}\text{NO}$ requires C, 79.16; H, 5.62; N, 7.10 %); n_{max} (KBr): C=N, 1575; Ar-OH, 1285; C=C, 1400 cm^{-1} ; ^1H NMR (DMSO) δ/ppm : 7.17-7.24 (3H, m, aromatic), 8.46 (1 H, s, CH), 10.15 (1 H, s, OH).

Electrodeposition of Mild Steel and Corrosion Test

A conventional three-electrode cell was used consisting of mild steel as working electrode, an Ag/AgCl electrode as reference electrode and platinum rod as counter electrode. The working electrode of mild steel was prepared by embedding the mild steel in epoxy resin and exposing a flat surface area of 1 cm^2 . The working electrode was abraded with a series of silica carbide paper from 320 grit up to 4000 grit, and then polished to mirror finish using diamond paste. Finally, it was washed with distilled water, degreased with acetone and left to dry in a desiccator.

The electrodeposition was carried out via chronoamperometry (CA) technique in alkaline bath solution containing L1a or L1b at 0.1 M concentration. All electrolytes were freshly prepared for each experiment. The corrosion behaviour of coated mild steel in 0.5 M NaCl was studied using Linear Polarization Resistance (LPR). Before the measurement, the working electrode was immersed in electrolyte for 15 minutes to obtain a steady state open circuit potential (OCP).

RESULTS AND DISCUSSION

The successful synthesis of L1a and L1b was indicated by the close agreement between the calculated and the experimental percentages of C, H and N. The signature IR peaks $n(\text{C}=\text{N})$ of azomethine were detected as strong bands at 1615 and 1575 cm^{-1} for L1a and L1b respectively.

Comparing these two compounds, it is interesting to note that the closer proximity of –OH to C=N in L1a, where the two functional groups are located *ortho* to one another, resulted in a stronger C=N bond indicated by the significantly higher IR absorption frequency than in L1b.

In the ¹H NMR spectroscopy, the presence of –OH in L1a and L1b is indicated by the chemical shift at 13.3 and 10.15 ppm respectively. The phenolic proton in L1a is highly deshielded by the C=N which is close to –OH, making hydrogen bonding possible. This causes the chemical shift to appear at the downfield region of 13.3 ppm, compared with the less deshielded –OH of L1b. Both the IR and NMR results showed intramolecular interaction between the hydroxyl and imine groups, especially for L1a.

Electrodeposition of L1a and L1b on Mild Steel

Chronoamperometry (CA) method was used to electrodeposit both compounds on mild steel. Figure 2 shows the chronoamperometric curves at three different potentials of 0.8 V, +1.05 V and +1.7 V based on the potential obtained from a cyclic voltammogram curves. CA was carried out in 0.3 M NaOH containing either 0.1 M L1a or 0.1 M L1b and recorded for 15 minutes of deposition. Current reduction was observed during the 15 minutes of deposition, particularly in the first minute.

For L1a, stationary current was achieved after about 5 minutes (300 seconds) for all deposition potentials used until deposition is completed. But for L1b, the stationary current was achieved after 10 minutes (600 seconds) for potentials at +0.8 V and +1.05 V, and 5 minutes (300 seconds) for +1.7 V. This shows that inhibitive layer of L1a forms faster than L1b. The suppression suggests that insulating properties of the film caused the disturbance of current flow causing current reduction (Genbour et al., 2000).

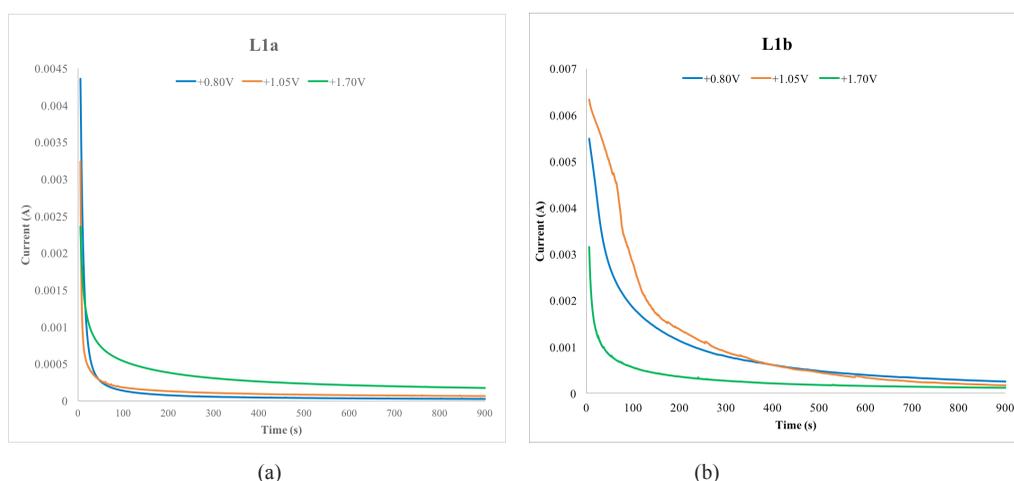
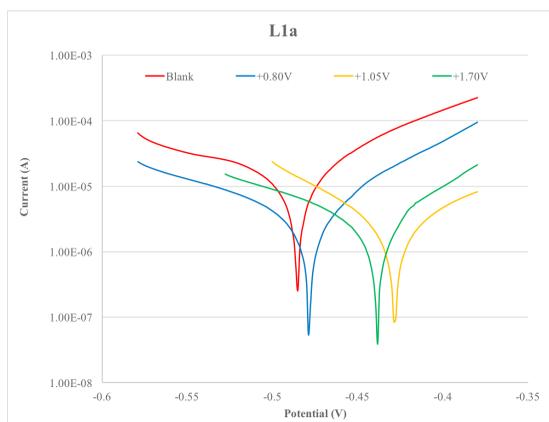


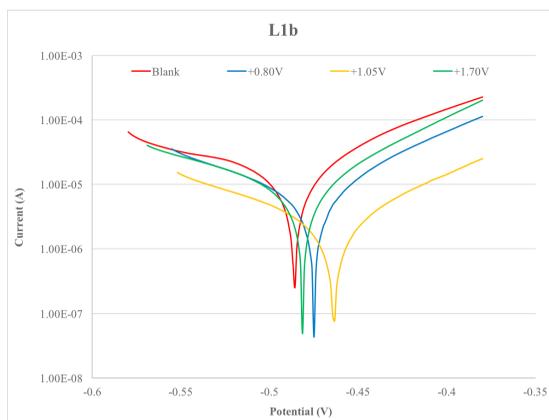
Figure 2. Chronoamperometric curves of deposition of: (a) L1a; and (b) L1b coatings on mild steel at three different deposition potentials

Potentiodynamic Polarization Measurements

The mild steel samples coated with L1a and L1b Schiff bases using chronoamperometry at three different deposition potentials were investigated for their corrosion inhibition efficiency. Figure 3 shows the Tafel polarisation curves of uncoated mild steel and mild steel coated with L1a (Figure 3(a)) and coated mild steel with L1b (Figure 3(b)) in 0.5M NaCl.



(a)



(b)

Figure 3. Tafel polarisation curves of uncoated and coated mild steel with: (a) L1a; and (b) L1b prepared at different deposition potential in 0.5M NaCl

Table 1 shows electrochemical parameters i.e. anodic Tafel slope (β_a), cathodic Tafel slope (β_c), corrosion potential (E_{corr}), corrosion current density (i_{corr}), corrosion rate (mm/yr), polarisation resistance ($k\Omega$) and inhibition efficiency (IE%). The inhibition efficiency of L1a and L1b Schiff bases was calculated using the following equation (Bagavathy & Ganesan, 2015):

$$IE\% = \frac{i_{corr}^o - i_{corr}}{i_{corr}^o} \times 100 \quad [1]$$

Where, i_{corr}^o and i_{corr} are uncoated and coated current densities, respectively.

Table 1
Corrosion inhibition of L1a and L1b on mild steel in 0.5 M NaCl

Compound	Potential (V)	β_a (mV/dec)	β_c (mV/dec)	E_{corr} (mV)	i_{corr} (mA/cm ²)	Corrosion rate (mm/year)	Polarisation resistance (k Ω)	Inhibition efficiency (%)
Blank	-	543.270	124.880	-485.120	35.3800	0.41111	1.24640	-
L1a	+0.8V	118.840	63.3960	-462.600	3.83920	0.044611	4.67660	90.34
	+1.05V	111.260	145.870	-412.950	4.62430	0.053734	5.92790	86.93
	+1.7V	672.330	121.150	-420.890	8.35880	0.097129	5.33360	76.37
L1b	+0.8V	187.510	90.0850	-443.780	10.7200	0.12457	2.46520	69.70
	+1.05V	196.520	117.580	-431.530	4.66170	0.054169	6.85370	86.82
	+1.7V	237.700	92.6370	-455.440	14.3040	0.16621	2.01170	59.57

From Figure 3(a), it is observed that current densities of the polarisation curves have decreased for all mild steel coated with L1a compared with the blank uncoated mild steel. For L1a, the inhibition efficiencies of all deposition potentials have defeated those of L1b. The highest inhibition efficiency was recorded by mild steel coated at +0.8 V with 90.34% efficiency corresponding to 0.044611 mm/yr corrosion rate. Meanwhile, data extracted from Figure 4(b) indicates that the inhibition efficiency of L1b is lower than that of L1a. The highest inhibition efficiency by L1b was recorded to be 86.82% which was mild steel coated at +1.05 V.

Thus, it can be concluded that the inhibitive film formed using the azomethine with hydroxyl group at *ortho* position (L1a) is more protective than the corresponding compound with hydroxyl group at *para* position (L1b). This shows that the L1a inhibitive film formed on the mild steel using low deposition potential deposited from bath solution provided more efficient corrosion protection than L1b.

Generally, both Schiff bases (L1a and L1b) have good corrosion protection efficiency for mild steel in 0.5 M NaCl. It may be associated with the presence of: (a) aromatic π electrons with conjugated double bonds; (b) π electrons of azomethine group; and (c) the electronegative heteroatom (N) bearing lone pairs of electrons present in both compounds. In addition, high inhibition efficiencies of both compounds are also due to the presence of hydroxyl substituent group on the aromatic ring.

Electron donating hydroxyl group has the inductive effect which enriches electron density and activates the aromatic ring and C=N, giving good absorptivity for the inhibitors. It was also found that the position of -OH in azomethine compound is shown to affect the corrosion inhibition efficiency. L1a has -OH at the *ortho* position while L1b has -OH at the *para* position of the aromatic ring. The closer proximity of -OH to C=N in L1a can activate the lone pair of electrons on N for adsorption on mild steel better than L1b. The mechanism of this effect is illustrated in Figure 4.

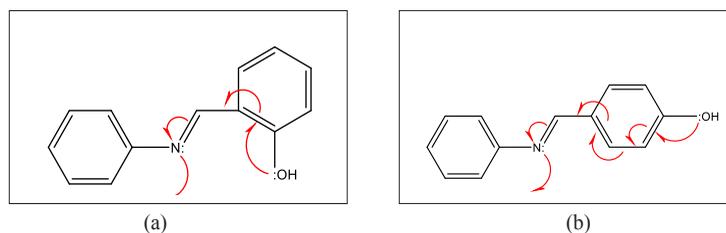


Figure 4. Mechanisms of inductive effect of: (a) L1a; and (b) L1b

This mechanism is strongly supported by the spectral evidence discussed above. The relatively strong C=N bond in L1a apparent in the higher IR frequency of 1615 cm^{-1} is in concordance with its more active role in adsorption to mild steel, resulting in stronger film coverage and better corrosion inhibition.

The lesser activated C=N in L1b due to the relative distance of -OH group showed a less efficient corrosion protection of mild steel. It is clear that intramolecular interaction between the -OH and C=N moieties in both compounds affect their corrosion inhibition properties.

CONCLUSION

Both Schiff bases, L1a and L1b, were successfully synthesised and characterised. Electrodeposition using chronoamperometry technique shows good formation of both films on mild steel surface. Corrosion inhibition studies using linear polarisation resistance show that both compounds have inhibition properties. The highest inhibition efficiency was mild steel coated with L1a at +0.8 V with 90.34% efficiency corresponding to 0.044611 mm/yr corrosion rate, while the inhibition efficiency of L1b Schiff base was lower than mild steel coated with L1a in 0.5 M NaCl. The highest inhibition efficiency by L1b was 86.82% with mild steel coated at +1.05 V. The position of hydroxyl group nearer the imine (*ortho* position) group in L1a activated the lone pair of N more effectively than L1b.

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