



Investigation of Substituent Effects on Corrosion Protection of Mild Steel by Schiff Bases in 0.5 M NaCl

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Abstract

Three Schiff bases, namely (*E*)-2-methoxy-6-((phenylimino)methyl) phenol (**A1**), (*E*)-2-(((4-chlorophenyl)imino)methyl)-6-methoxyphenol (**A2**) and (*E*)-2-(((4-bromophenyl)imino)methyl)-6-methoxyphenol (**A3**), were synthesised via condensation reaction between *o*-vanillin and derivatives of aniline. The structures were elucidated through spectral and physicochemical techniques of melting point, elemental analysis (C, H and N), ¹H Nuclear Infrared (IR) spectroscopy, Magnetic Resonance (NMR) and UV-Visible Spectroscopy. The distinctive $\nu(\text{C}=\text{N})$ were observed in range of 1610-1613 cm^{-1} while $\nu(\text{OH})$ peaks appeared between 13.37-13.44 ppm. 0.05 M solutions of the Schiff bases were prepared in 0.3 M aqueous NaOH solution prior to depositing on mild steel using cyclic voltammetry (CV) technique, forming brownish coloured Schiff base coatings. The corrosion behaviour of coated and uncoated mild steel was studied using Tafel Extrapolation Method (TEM) in 0.5 M NaCl. The mild steel coated with A1 showed the highest inhibition efficiency (I.E.) of 84.81%, hence indicating a superior surface coverage, followed by A2 and A3 with 67.48% and 54.82 % I.E., respectively.

Keywords: Schiff base, Electrodeposition, Cyclic voltammetry, corrosion inhibition, mild steel.

1. Introduction

Corrosion is accelerated by the presence of electrolytes such as salts, hence offshore and seaside metal structures are particularly vulnerable. The combination of moisture, oxygen and salt such as sodium chloride (NaCl) can bring severe damage to metals. The attack may be due to chloride ions contained in seawater. Sodium chloride (NaCl) solution has been reported as an aqueous corrosion medium in many studies [1,2,3]. The use of sodium chloride solution is also widely applicable in various systems such as cooling systems, storage reservoirs and pipelines for water and fuel [4].

One of the techniques that can be used to overcome this issue is by using organic coatings such as Schiff bases either by using it as corrosion inhibitors or by electrodeposited inert films. Schiff bases are well known compounds that contain nitrogen (N), commonly accompanied with sulphur (S) and/or oxygen (O) atoms [5]. Schiff bases are characterized by C=N functional group(s) containing lone pair of electrons on the imine N that can act as anchoring points on metal surface, facilitating physisorption or chemisorption, forming protective monolayer of molecules against corrosion agents [6]. This corrosion protection is enhanced by planarity of molecules, a property that can be relatively easily designed into the Schiff bases to increase the adsorption on the active sites of metal surface, as reported by several authors [7,8,9]. The presence of electron rich moieties such as aromatic rings and other heterogeneous atoms like O and S as well as halides are desirable for adsorption.

The adsorption and bonding between compounds and metal substrate will protect mild steel from corrosion more effectively [10]. A number of Schiff bases has been reported as corrosion inhibitors [11,12], however very inadequate exploration on electrodeposited

Schiff bases on metal substrate for corrosion prevention [3,13]. Researchers commonly use electrochemical methods to electrodeposit metal on other metal surface such as copper on stainless steel substrate [14]. Thus, it is interesting to explore electrodeposition properties of simple Schiff base compounds to investigate the inhibiting ability of the compound by forcing it bind on mild steel surfaces using electrodeposition techniques.

Previous studies have reported the use of Schiff bases, both as inhibitors and electrodeposited coatings, using different concentrations of Schiff bases and varying the temperature of solution and period of exposure of coated metal substrate in corrosive media. This paper focuses on investigating the best inhibiting compound using CV as electrodeposition technique, supported by corrosion studies carried out using TEM. The synthesis and characterization of three Schiff bases A1, A2 and A3 having very similar chemical structures except for the presence of -Cl in A2 and -Br in A3 (Fig. 1) are described. The difference of inhibition properties of the compounds is explained based on the chemical structures of A1, A2 and A3.

2. Methods

2.1. Synthesis of A1, A2 and A3

o-vanillin (20 mmol) was dissolved in absolute ethanol (15 mL) and stirred until fully dissolved. Aniline, and its Cl- and Br- derivatives for A2 and A3, respectively, (20 mmol) were added slowly into the ethanolic *o*-vanillin solution. The mixture was refluxed for 3 hours to produce orange precipitate. The precipitate was filtered off after slow cooling to room temperature and washed thoroughly with cold ethanol. It was air dried, weighed and kept in a desiccator.

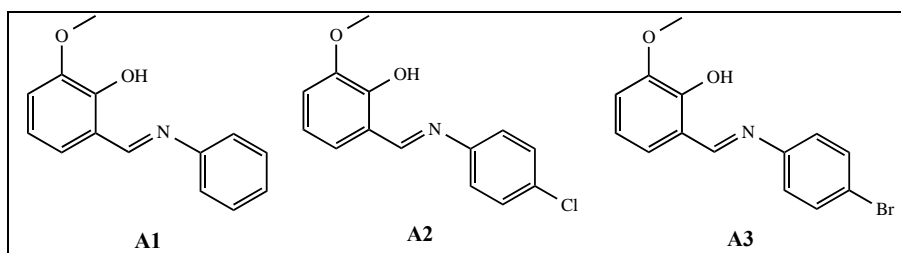


Fig. 1: Chemical structure of A1-A3

2.2. Electrodeposition of Schiff base and Corrosion Test

The electrodeposition technique and corrosion studies were adopted by method done by [15] with slight modification on the concentration of each compound that was set at 0.05 M.

3. Result and Discussion

3.1 Synthesis and characterization

The physicochemical properties of all compounds are tabulated in Table 1. The successful synthesis of all the orange colored Schiff bases A1-A3 were indicated by the close agreement between the experimental percentages of C, H and N with the theoretical values. The compounds were produced in good yields ranging between 83-91 % with quite narrow ranging or sharp melting points. The increase in melting points is directly proportional with molecular mass of the compounds. Coupling the elemental analysis results with the sharp melting points, it could be suggested that the compounds isolated were of high purity.

Table 1: Physicochemical properties of A1-A3

Compound	Molecular formula (RMM)	Yield (%)	Melting point (°C)	Colour	Elemental analysis (%)		
					Experimental (Theoretical)		
					C	H	N
A1	C ₁₄ H ₁₃ NO ₂ (227.26)	83.16	90-92	Orange	73.99 (73.99)	5.54 (5.77)	5.92 (6.16)
A2	C ₁₄ H ₁₂ ClNO ₂ (261.71)	86.94	111-113	Orange	64.40 (64.25)	4.49 (4.62)	5.07 (5.35)
A3	C ₁₄ H ₁₂ BrNO ₂ (306.16)	91.13	122-124	Orange	55.17 (54.92)	3.82 (3.95)	4.18 (4.58)

3.2 FTIR Spectroscopy

A comparison between important IR data of all Schiff bases with their respective starting materials was made and presented in Table 2. It was interesting to observe the appearance of new peaks in the region of 1610-1617 cm⁻¹ assignable to C=N accompanied by the disappearance of the C=O peaks in the region of 1638 cm⁻¹ of the aldehydes. The N-H peak observed at 1621 cm⁻¹ of aniline does not appear in any of the Schiff bases. This N-H peak represents amine bond of N-H₂ that was broken down upon condensation, with the removal of H₂O. Thus, N of amine combined with C from carbonyl to form the signature bond of C=N of Schiff bases in concordance with the disappearance of NH bend at 1621 cm⁻¹.

3.3 NMR Spectroscopy

All three compounds have methoxy substituent at the aldehyde moiety, with the difference of presence of Cl and Br for A2 and A3, respectively, as shown in Table 3. As stated by [16], compounds with methoxy moieties exhibit a weak and relatively sharp, characteristic peak in the region of 2860-2800 cm⁻¹. The methoxy peaks for compounds A1, A2, and A3 were observed at 2838 cm⁻¹ which is exactly the same frequency as methoxy peak in the starting material of *o*-vanillin. In A2 and A3, the presence of Ar-Cl and Ar-Br was shown by medium peaks at 734 cm⁻¹ and 505 cm⁻¹, respectively.

Table 2: FTIR assignments of A1-A3

Type	Compound	(C=N)	(C=O)	(N-H) bend	(C-N)	□O-H)	(O-CH ₃)	(Ar-X)
Starting materials	<i>o</i> -vanillin	-	1638	-	-	3011	2838	-
	Aniline	-	-	1621	1254	-	-	-
Ligand	A1	1613	-	-	1254	3077	2838	-
Starting materials	<i>o</i> -vanillin	-	1638	-	-	3011	2838	-
	4-choloraniline	-	-	1621	1287	-	-	735
Ligand	A2	1613	-	-	1254	3077	2838	734
Starting materials	<i>o</i> -vanillin	-	1638	-	-	3011	2838	-
	4-bromoaniline	-	-	1621	1284	-	-	503
Ligand	A3	1610	-	-	1254	3049	2838	505

Table 3: ¹H NMR data and assignment for A1-A3

Compound	Structure	-C ⁸ =NH	-C ¹ -OH	-O-CH ₃	C-H Aromatic (A)	C-H Aromatic (B)
A1		8.66 1H, s	13.37 1H, s	3.97 3H, s	6.89-6.96 3H, m J= 7.85-7.88	7.29-7.49 5H, m J= 7.75

A2		8.63 1H, s	13.44 1H, s	3.96 3H, s	6.89-7.07 3H, m J=7.25-7.89	7.22-7.44 4H, m J=8.64
A3		8.62 1H, s	13.43 1H, s	3.96 3H, s	6.88-7.07 3H, m J=7.28-7.88	7.15-7.60 4H, m J = 8.46- 8.48

Based on Table 2, the position of -OH peak is at downfield region due to the proton that attached directly to oxygen, an electronegative atom that withdraws electron from the proton, lowering of electron density and exposed the proton nucleus to the magnetic field i.e. deshielding effect. The peaks for azomethine proton HC=N for A1-A3 were observed in the range of 8.63-8.66 ppm, slightly lower than that expected for a HC=O, commonly reported at 9.00-10.00 ppm (Pavia et. al, 2015). This lowering corresponds to the lower electronegativity of N than O causing less deshielding effect. The peaks for aromatic protons in all compounds appear in the range of 6-9 ppm due to the anisotropic effect of the π -electrons. They display spin-spin splitting pattern with coupling constant J value of around 6-9 Hz, typical of the interaction of two *ortho*-hydrogens. However, all three compounds give similar spectrum except for the presence of Cl and Br at the aniline moieties of A2 and A3, respectively, indicating that the Cl and Br substituents did not produce much shielding effect to their neighbouring protons.

3.4. UV-Visible Spectroscopy

The electronic spectra of compounds dissolved in acetonitrile (ACN) were recorded from 200-900 nm and tabulated in Table 4. Peaks were observed below 400 nm indicating the absorption of

UV light. No peaks were detected beyond 400 nm indicating that there was no visible light absorption occurring in the compounds. Based on Fig. 2, three main absorption peaks were observed for all ligands, due to electronic transitions of $\pi \rightarrow \pi^*$ for C=C in aromatic rings, $\pi \rightarrow \pi^*$ for -C=N and $n \rightarrow \pi^*$ for -C=N.

The absorption of light in the UV or visible region corresponds to transitions of electrons from lower energy orbitals of non-bonding (n) orbitals or π orbitals onto the higher energy level orbital of π^* [17]. Strong absorption peak for $\pi \rightarrow \pi^*$ electronic transition for aromatic C=C appeared in the range of 228-231 nm for all compounds. These values are in good agreement with the values previously reported by [18]. The $\pi \rightarrow \pi^*$ electronic transitions for C=N chromophores were observed at wavelength range of 281-282 nm. These peaks were slightly higher than the $\pi \rightarrow \pi^*$ for aromatic rings with medium adsorption peak.

Transitions of $n \rightarrow \pi^*$ occurred in the range of 313-318 nm, appearing as strong adsorption peaks. This transition explains about the movement of electrons from lone pairs of nitrogen to unoccupied orbital of π^* . All these values are concordance with value reported by [19, 20]. The $n \rightarrow \pi^*$ transitions showed higher wavelengths because the energy gap between the non-bonding and π^* orbitals is lower than that between π and π^* orbitals.

Table 4: UV-Visible spectral data for electronic transitions of A1-A3

Compounds	Transition	λ_{max} (nm)	Absorbance	Molar absorptivity, ϵ
A1	$\pi \rightarrow \pi^*$ (C=C)	228	1.48997	14899.7
	$\pi \rightarrow \pi^*$ (C=N)	282	0.8325	8325.0
	$n \rightarrow \pi^*$ (C=N)	313	0.89891	8989.1
A2	$\pi \rightarrow \pi^*$ (C=C)	231	1.60669	16066.9
	$\pi \rightarrow \pi^*$ (C=N)	282	0.97734	9773.4
	$n \rightarrow \pi^*$ (C=N)	317	1.15488	11548.8
A3	$\pi \rightarrow \pi^*$ (C=C)	230	1.63473	16247.3
	$\pi \rightarrow \pi^*$ (C=N)	281	1.01077	10107.7
	$n \rightarrow \pi^*$ (C=N)	318	1.22053	12205.3

Electrodeposition of A1-A3

Referring to cyclic voltammograms in Fig. 3, all compounds revealed similar trend for the first cycle where the current initially increased to a maximum, then decreased. A1 contains two electron rich groups of hydroxyl and methoxy while A2 and A3 contain electron withdrawing substituents Cl and Br, respectively. For compound A1, the maximum current was lower (0.0106 A) than that of A2 (0.037 A) and A3 (0.028 A) indicating that A1 required less current for deposition on mild steel surface, a sign of higher affinity to electropositive mild steel.

The second cycle of A1 recorded a low current reading of almost 0 A with no maximum current peak shown in Fig. 3 (a). This behaviour revealed that even after the first cycle, an almost perfect surface coverage of mild steel by A1, thus prevent any electron transfer to occur. Nevertheless, for A2 and A3, the magnitude of cur-

rent suppression decreased progressively from the second to fifth cycle. This denotes that the existence of halogens groups affects the deposition of both compounds where active sites of anode (mild steel) slowly became passivated after the first cycle, reducing electron transfer. Orange-brownish films were observed in all coated mild steels using A1, A2 and A3.

3.5. Tafel Extrapolation Method

The analysis of coated mild steel in corrosive medium was done using Tafel Extrapolation Method. Anodic and cathodic polarization curves of all compounds were compared with uncoated mild steel that acted as blank. The corrosion protection of mild steel in 0.5 M NaCl has been improved after the mild steel electrode was coated with Schiff bases. The related 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), polarization resistance ($k\Omega$) and inhibition efficiency ($\text{IE}\%$) are summarized in table of each compounds in Table 5.

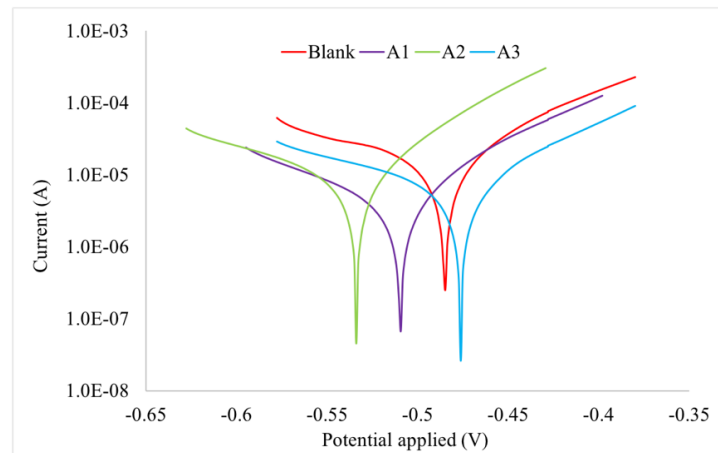


Fig. 2: Tafel plot of uncoated (blank) and coated mild steel using A1-A3

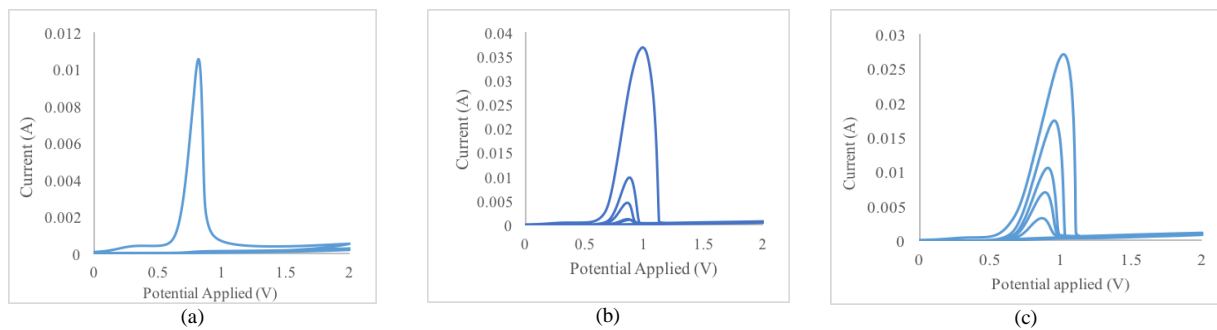


Fig. 3: Electrodeposition of (a) A1, (b) A2 and (c) A3 using CV

Table 5: Tafel Extrapolation results of uncoated and coated mild steel with A1-A3.

Label	β_a (mV/dec)	β_c (mV/dec)	E_{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion rate (mm/year)	Polarization Resistance ($k\Omega$)	Inhibition Efficiency (%)
Blank	672.97	127.95	-486.01	37.45	0.435	1.247	-
A1	166.37	72.89	-509.76	5.68	0.066	3.871	84.81
A2	194.26	71.70	-533.83	12.18	0.142	1.868	67.48
A3	781.06	127.73	-477.22	16.92	0.197	2.818	54.82

The formation of Schiff base films on mild steel lead to changes in Tafel slopes of polarization curves, which resulting in the decrease of corrosion current densities (i_{corr}) and also the increase in corrosion potential (E_{corr}), through interference at anodic and cathodic reactions. From Table 5 it can be observed the presence of coatings shifted the anodic and cathodic curves to lower current. This indicates the layer coated on mild steel can hinder both anodic dissolution of mild steel as well as oxygen reduction at cathodic sites in corrosion prevention process [21]. The coatings also can be described as mixed-type coatings which anodic effectiveness were predominant than cathodic as shown by β_a and β_c values.

The corrosion current densities (i_{corr}) were shifted to lower values which are less than i_{corr} for blank ($37.4460 \mu\text{A}/\text{cm}^2$) for all coated mild steels. A decrease in i_{corr} had been reported to cause an increase in inhibition efficiency due to an increase in the blocked fraction of the mild steel surface by adsorption of the compounds [22]. The lowest inhibition efficiency, IE, of 54.82 % was recorded for mild steel coated with A3 while the highest of 84.81 % was observed for mild steel coated with A1. This was a firm indication of the formation of a stable adsorbed A1 layer on the mild steel surface using CV.

4. Conclusion

Several conclusions of the study can be drawn as follows. The formation of protective layer of all Schiff bases A1, A2 and A3 on

mild steel substrate retarded or slowed down the corrosion. Compound A1 displayed the best protective coatings against corrosive medium with inhibition efficiency of 84% as compared to A2 and A3.

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