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Research paper

Corrosion Retardation of Mild Steel Electrodeposited with 4-hydroxybenzalaniline in 0.5 M NaCl

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Abstract

The synthesis of a Schiff base, 4-hydroxybenzalaniline (4-HB) was carried out via condensation reaction giving 81.7% yield. 4-HB was characterized via physicochemical and spectroscopic techniques namely melting point, microelemental analysis (C, H and N), Proton Nuclear Magnetic Resonance (^{1}H NMR) and Infrared (IR) spectroscopy. The characteristic □(C=N) peak was observed at 1613 cm^{-1} and the □(OH) at 10.15 ppm. Cyclic voltammetry (CV) and chronoamperometry (CA) techniques were employed to electrodeposit 4-HB on mild steel with 0.1 M inhibitor concentration in 0.3 M NaOH. The formation of a yellow imine film was observed on the mild steel. The corrosion behavior of uncoated and coated mild steel was investigated using Tafel Extrapolation Method (TEM) and Electrochemical Impedance Spectroscopy (EIS) in 0.5 M NaCl corrosion medium. The coated mild steel showed more superior corrosion resistance than the uncoated one. The mild steel coated with 4-HB through CA technique at potential +1.50 V revealed the highest inhibition efficiencies of 97.71 % and 96.79 % for EIS and TEM investigations, respectively, indicating a good surface coverage. The Schiff base revealed potent organic corrosion inhibition activity and has a high potential for commercialization.

Keywords: *Chronoamperometry; Corrosion inhibition; Cyclic Voltammetry; Electrodeposition; Schiff base.*

1. Introduction

Corrosion has become the major concern where huge attention had been focused on the damage and destruction of metallic structures where the effects of corrosion catastrophe can be very severe. Countless methods to curb this problem had been explored including surface coating using organic compounds. Studies had shown that organic compounds such as Schiff bases can be used as effective anti-corrosion coatings for carbon steel and copper in sodium chloride solution [1,2].

The considerations to choose a good coating are mainly based on two characteristics; firstly, the compound must be synthesised from relatively inexpensive starting materials; secondly, the compound must be rich in electrons or have electronegative atoms [3]. An important characteristic of a good coating material is the abundance of active centers or donor atoms. It must have the capability to form bonds with the metal surface where electron transfers occur, in which metal acts as an electrophile and the inhibitor acts as a Lewis base, whose nucleophilic centers are O and/or N atoms with lone electron pair(s) available for sharing [4,5]. There is a number of Schiff bases that have been reported to have good corrosion inhibiting properties [6,7]. However very few explorations on electrodeposited Schiff bases on metal substrate in preventing corrosion have been reported [8,9]. Researchers have described Schiff bases along with deposition technique for a number of studies such as electrodeposited Schiff base complexes on gold template and applied as dopamine sensing [10]; and investigation using Schiff base cobalt complexes as effective water oxidation catalyst [11]. Thus, it is pertinent to probe on the electrodeposition properties of simple Schiff base compounds to learn the mechanism of binding of these compounds by electrochemically driving them to bind on mild steel surfaces using electrodeposition techniques. This paper is focused on investigating the better electrodeposition techniques between CV and CA; and to study the performance of Schiff base coatings obtained at different potentials when using CA. These corrosion studies were carried out using TEM and EIS.

2. Materials and methods

2.1. Materials

All the chemicals and solvents used were of analytical grade. 4-hydroxylbenzaldehyde, aniline, absolute ethanol, deuterated chloroform, and potassium bromide (KBr) were purchased from commercial suppliers and used without further purification. The microanalytical data (C, H and N) of the compound were obtained from Thermo Scientific Flash 2000 Elemental Analyzer. Melting points were determined using Stuart SMP10. Perkin-Elmer model 1750 X FTIR spectrophotometer using KBr pellets was employed to record Infrared (IR) spectra of compounds in range of 4000-450 cm^{-1}. ^{1}H NMR spectra were analyzed on a Bruker Varian-600 MHz spectrometer using deuterated chloroform and expressed in parts per million (□□ ppm). Morphology study of the coated and uncoated mild steel coupons were performed on FESEM Zeiss Supra 40P.

2.2. Synthesis and characterization of 4-hydroxybenzalaniline (4-HB)

Fig. 1 shows the expected structure of (4-HB). The method employed to synthesis 4-HB was adopted from [8,9]. A mixture of 20 mmol of 4-hydroxylbenzaldehyde 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%).

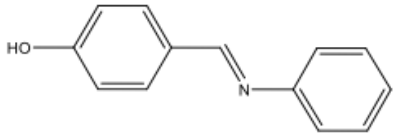

Fig. 1: The structure of 4-hydroxybenzalaniline

2.3. Surface Morphology using Field Emission Scanning Electron Microscope (FESEM)

Polished mild steel with dimension of 1 cm x 2 cm was used in this study and the exposed area was 1 cm x 1 cm for coating. The mild steel specimen was coated with 4-HB using the two different electrodeposition techniques. After deposition, the coated mild steel was rinsed thoroughly with absolute ethanol and left to dry in a desiccator to be moisture-free prior to SEM analysis to prevent water adsorption that might produce false results.

2.4. Electrodeposition and Corrosion Studies

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 electrodes were abraded with a series of silica carbide paper from 320 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 cyclic voltammetry (CV) and chronoamperometry (CA) techniques in alkaline bath solution containing 4-hydroxylbenzalaniline of 0.1 M concentration. In chronoamperometry (CA) method, three different potentials of +0.8 V, +1.50 V and +1.7 V, was set to electrodeposit 4-hydrobenzalanaline based on the potential cycles. All electrolytes were freshly prepared for each experiment. The corrosion behavior of coated mild steel in 0.5 M NaCl were studied using Tafel Extrapolation Method (TEM) and Electrochemical Impedance Spectroscopy (EIS).

In Tafel Extrapolation Method (TEM), the related electrochemical parameters i.e. anodic Tafel slope (β_a), cathodic Tafel Slope (β_c), corrosion potential (E_{corr}), corrosion current density (ι_{corr}), corrosion rate (mm/yr), polarization resistance (kΩ) and inhibition efficiency (IE%) are summarized in Table 2. The inhibition efficiencies was calculated using equation 1 [12]:

$$IE\% = \frac{i^{\circ}_{corr} - i_{corr}}{i^{\circ}_{corr}} \times 100 \quad (1)$$

where, i°_{corr} and i_{corr} are uncoated and coated current densities, respectively.

EIS were carried out using AC signal (10 mV) peak to peak at the open circuit potential (OPC) for 15 minutes with the frequency form lowest to highest value in range of 100 kHz to 0.1 Hz. Before the measurement, the working electrode was immersed in electrolyte for 15 minutes to obtain a steady state open circuit potential (OCP). The inhibition efficiency of mild steel was calculated using equation 2 [13]:

$$IE\% = \frac{R_{ct(coated)} - R_{ct(blank)}}{R_{ct(coated)}} \times 100 \quad (2)$$

where R_{ct} indicates the charge transfer.

3. Result and discussion

3.1. Synthesis and Characterization of 4 hydroxybenzalaniline

All physicochemical properties of 4-HB were tabulated in Table 1 where successful synthesis of Schiff base was tentatively indicated by the close agreement between the experimental percentages of C, H and N with the theoretical ones. The melting point of the compound was quite high at 196-198 °C. This can be explained by the fact that the structure of 4-HB is quite open, having –OH at *para*-position allowing extensive intermolecular H-bonding to occur. Thus, high amount of energy is needed to melt it. This result was supported with the report by [14] stating that among aromatic compounds, *para*-derivatives usually melt at higher temperatures than that corresponding *ortho*- and *meta*-derivatives. Coupling the elemental analysis results with the narrow-range melting point, it could be suggested that the compound isolated was of high purity.

3.2. Electrodeposition of 4-hydroxybenzalaniline on Mild Steel

In cyclic voltammetry (CV) techniques, the scan potential range used was set to start from 0 V to +2 V and back to 0 V with a scan rate of 0.1 V/s. Five CV cycles were performed to coat 0.1 M concentration of 4-HB on mild steel surface as shown in Fig. 2. A yellow thin film was observed on the mild steel surface at the end of the cycles. CV was carried out in 0.3 M NaOH solution at room temperature. Current suppression was observed that indicates the current was reduced after the first cycle. This denotes that the active sites of anode (mild steel) started to become passive after the first cycle, reducing electron transfer and decreasing electrodeposition [15].

In chronoamperometry (CA) method three different potentials of 0.8 V, +1.50 V and +1.7 V, was set to electrodeposit 4-HB based on the potential cycles obtained from the cyclic voltammetry curves (Fig. 3). The three potentials were chosen to observe the dispersion of coating at the beginning, at the highest peak and at the end of the cycle. CA was carried out in 0.3 M NaOH that contained 0.1 M concentration of 4-HB, recorded for 15 minutes of each potential deposition. Current reduction was detected during the 15 minutes of deposition.

Stationary current was achieved after about 10 minutes (600 seconds) for all deposition potentials used until deposition was completed. The stationary current was achieved after 400 seconds for potentials +0.8 V, 300 seconds at potential +1.50 V, and less than 60 seconds for +1.7 V. The current suppression suggested that the insulating properties of the film caused the disturbance of current flow causing current reduction [16]. Based on Fig. 3, it is apparent that the good protective properties by 4-HB are characterized by low anodic current densities at a constant applied potential at three different potential due to formation of Schiff bases layer. It can be concluded that the films form using CV and CA techniques were expected to protect mild steel in corrosive in which were test using TEM and EIS methods.

Table 1: Physicochemical properties of 4-hydroxybenzalaniline

Molecular formula (RMM)	Yield (%)	Melting point (°C)	Colour	Elemental analysis (%) Experimental (Theoretical)		
				C	H	N
C_{13}4-HB_1NO (197.24)	81.65	196-198	Light yellow	78.15 (79.16)	5.58 (5.62)	6.90 (7.10)

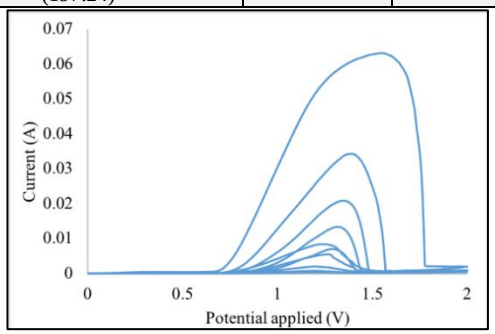

Fig. 2: Eletrodeposition of 4-HB on metal forming cyclic voltammograms of potential range 0 V- (+2 V) – 0 V

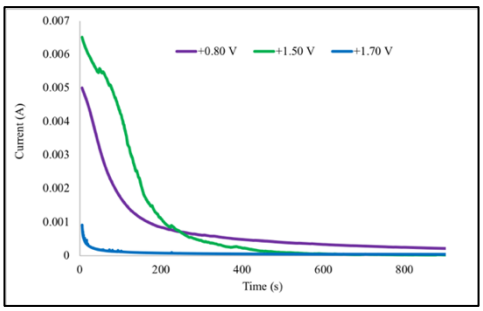

Fig. 3: Eletrodeposition of Chronoamperometric curves at three different potentials

3.3 Surface studies using FESEM

The confirmation on the presence of coating of both compounds on mild steel was supported by the analysis using FESEM. It was observed that the corroded mild steel revealed a rougher surface than the coated mild steel surface that appeared smoother. This shows that the coatings via all three potential tended to form protective adsorbed films on the surface of the metal, hence protecting the metal against corrosion. However, the mild steel coated via CA at potential +1.50V gave the best surface coverage. The corresponding FESEM images with 5000x magnification are presented in Fig. 4.

3.4 Tafel Extrapolation Method (TEM)

Based on Table 2, a decrease in I_{corr} from 73.38 □A/cm^2 (blank) to 5.77 □A/cm^2 had been noted, causing an increase in inhibition. Riggs (1973) had reported the classification of compound as coating whether it is anodic or cathodic type is feasible when displacement of corrosion potential (E_{corr}) is more than ±85 mV with respect to corrosion potential of blank. In this study, the change in E_{corr} and +96.68 mV which can be classified as anodic type inhibitor [17], thus, affect anodic reaction or metal dissolution. Based on the tabulated data, it is also observed that β_a value was more affected for both compounds than β_c, which indicates that an anodic reaction was more affected.

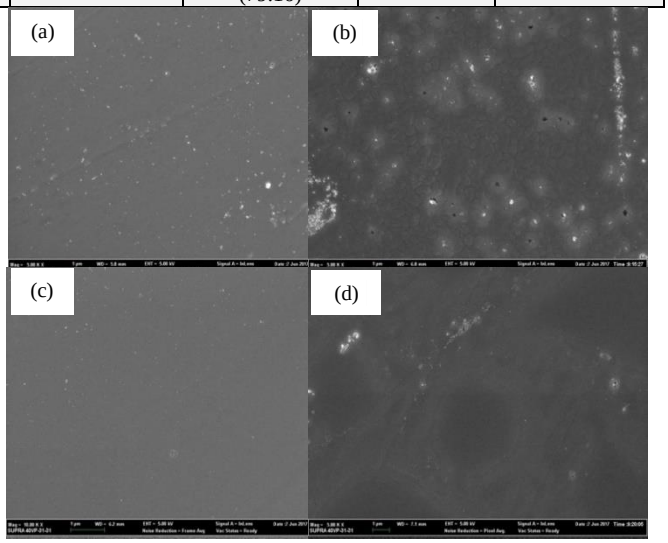

Fig. 4: SEM micrographs of (a) mild steel coated by CV (b) mild steel coated by CA at potential +0.80 V (c) mild steel coated by CAat potential +1.50 V (d) mild steel coated by CA at potential +1.70 V (Magnification: 5000x)

All data of Tafel Extrapolation results of corrosion behaviour of mild steels coated using CA technique were presented in Table 2. From the data, both βa and βc were affected indicating that both anodic and cathodic reactions were affected. Based on the chronoamperometric curves plotted in Fig. 3, there was no significant shifting of E_{corr} that can be seen from for corrosion potential (E_{corr}). The displacement of corrosion potential (E_{corr}) for all coated mild steel was still within ±85 mV with respect to the corrosion potential of blank. Thus, the coatings using CA can be assigned as mixed type inhibitor coatings.

The current densities (i_{corr}) for all coated mild steel using both techniques were slightly lower than the blank. This also indicated that the coatings allowed less current to penetrate onto the mild steel surfaces, and thus protecting the metal from the corrosive medium. The highest inhibition efficiency (IE) was observed for coatings prepared via CA at +1.50V, shown in Fig. 5(b). The stability of ligand-metal ion interface in acidic medium enabled the formation of a protective layer on the surface which resisted the attack of NaCl solution [17]. This shows that the deposition of 4-HB using CA method afforded a better coverage than that of the CV method.

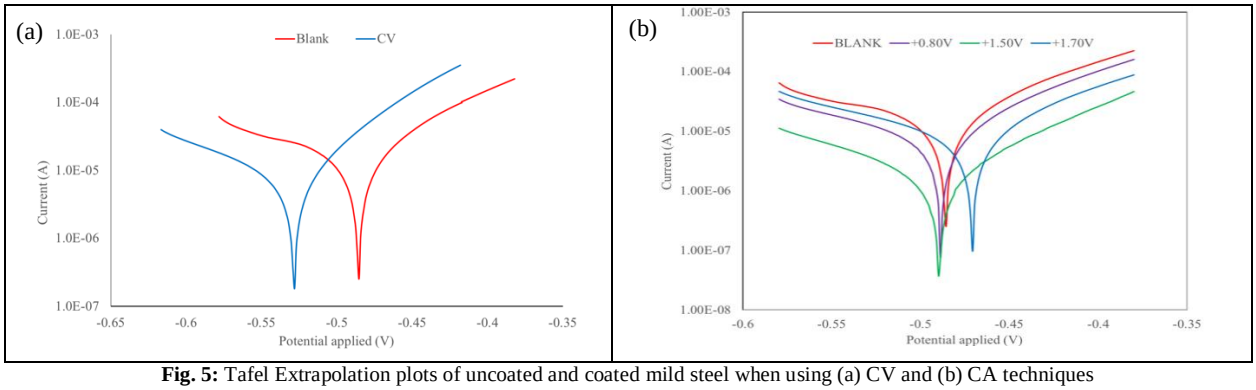

Fig. 5: Tafel Extrapolation plots of uncoated and coated mild steel when using (a) CV and (b) CA techniques

Table 2: Tafel Extrapolation results of uncoated and coated mild steel

Label	Potential	β_a (mV/dec)	β_c (mV/dec)	E_{corr} (mV)	i_{corr} (□A/cm^2)	Corrosion rate (mm/year)	Polarization resistance (kΩ)	Inhibition efficiency (%)
Blank	-	465.49	292.84	-535.01	73.38	0.853	1.064	-
CV	(0-2-0)	198.76	121.65	-438.99	5.77	0.067	5.678	92.13
CA	+0.80	417.98	95.85	-501.01	14.64	0.170	2.312	80.04
	+1.50	**140.68**	**87.73**	**-407.21**	**2.39**	**0.028**	**9.837**	**96.79**
	+1.70	402.99	109.55	-497.37	15.95	0.185	2.346	78.27

3.5 Electrochemical Impedance Spectroscopy (EIS)

The related electrochemical impedance parameters such as electrolyte resistance (R_s), charge transfer resistance (R_{ct}), and constant phase element for passive film (CPE) are tabulated in Table 3. The yellow thin film on mild steel surface that was observed after both electrodeposition techniques using CV and CA were also studied using electrochemical impedance spectroscopy (EIS). Through this test, the behavior of coated and uncoated mild steel against corrosion medium of 0.5 M NaCl was analyzed. Fig. 6 shows the Nyquist plot of EIS data.

Table 3: Electrochemical Impedance Spectroscopy (EIS) results of uncoated and coated mild steel

Label	Potential	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	CPE (mF)	Inhibition efficiency (%)
Blank	-	-21.3	28.8	0.0323	-
CV	(0-2-0)	7.22	684	33	95.78
CA	+0.80	7.45	837	46.2	96.56
	+1.50	**7.96**	**1260**	**3.96**	**97.71**
	+1.70	10.7	631	341.1	95.43

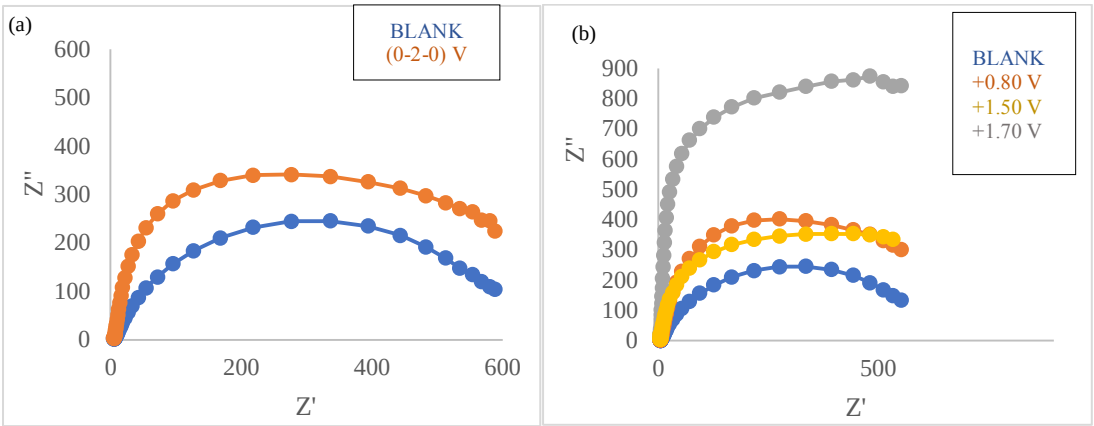

Fig. 6: (a) Nyquist plots of blank and coated mild steel using CV at potential range (0-2-0) V; (b) Nyquist plot of blank and coated mild steel using CA techniques at three different potentials

A proposed chronology of events of Schiff base coating formation on mild steel substrate during the entire CV scanning from 0 V to +2 V back to 0 V in 0.3 M NaOH solution is illustrated in Fig. 7. At the beginning of the scan, no current density was observed indicating that there was no reaction occurring on the mild steel surfaces, thus, no formation of films. The anodic current density (reduction) started to increase at potential +0.60 V and reached the maximum current peak. As the current increased, the anodic current was under electron transfer control where a film of the compound was starting to form on the mild steel surface. At the maximum current peak, the coating was presumed to have been deposited and started forming layer under mixed electron transfer and mass transport control. Then, the anodic current density started to decrease, a process controlled by mass transport. However, the decrease may be correlated with reduction of compound species at the interface of mild steel electrode which indicates that there was a nucleation process and growth which were also controlled by mass transport and diffusion.

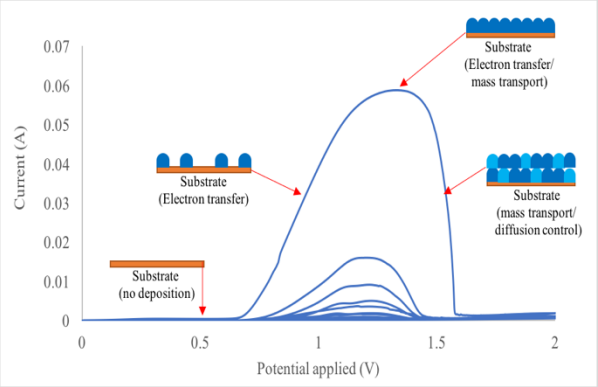

Fig. 7: Proposed mechanism of Schiff base coating on mild steel during cyclic voltammetry (CV)

However, on the reverse scan from +2.0 V back to 0 V, less or no growth occurred because there was no current density or peak that could be observed from the voltammograms. Thus, it can be concluded that there was no cathodic current (oxidation) formed on the reverse scan.

It is interesting to note that the inhibition efficiency of the compound in corrosive medium appeared to give the best retardation values when the potentials were chosen at the highest peak of cyclic voltammograms. At highest peak of the cyclic voltammograms the best surface coverage was formed affording the highest inhibition efficiency. At potential +0.80 V, the structure showed some micropores which indicates that the potential supply was not enough to drive a full surface coverage of the mild steel surface. However, for potential +1.70 V, the inhibition efficiency based on the TEM and EIS were lower than that for +1.50V. This observation might be due to the adsorption of oxygen on the mild steel surface where the oxygen evolved at high potential. Thus, it can be intimated that both oxygen and 4-HB were competing to be adsorbed on the metal substrate.

4. Conclusion

Electrodeposition of 4-HB on mild steel using CV and CA techniques showed the formation of imine films on mild steel surface. Coating using CA techniques gave a better coverage of compound on mild steel surface than using CV. Electrodeposited film of the compound successfully retarded corrosion of mild steel. The best inhibition efficiency (IE) was observed for mild steel coated with 4-HB using CA at potential +1.50V with IE of 96.79 % and 97.71% when investigated using TEM and EIS, respectively.

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