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Synthesis and Anticorrosion Studies of Azomethine Derived from Aniline

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Two series of azomethine compounds derived from 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin) with 3-nitroaniline and *p*-toluidine were synthesized through condensation and characterized. The synthesized compounds were elucidated via elemental analysis (CHNS), nuclear magnetic resonance (NMR) spectroscopy, and infrared (IR) spectroscopy. The corrosion inhibitory effects of two azomethine compounds, namely 2-methoxy-6-((*p*-tolylimino)methyl)phenol (A3) and 2-methoxy-6-(((3-nitrophenyl)imino)methyl)phenol (A4) were studied on mild steel in 1 M hydrochloric acid (HCl) by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. Based on the electrochemical measurements, azomethine compounds A3 and A4 demonstrated good inhibition efficiency (87%) on mild steel in an acidic environment. The surface morphology of the mild steel specimen was further investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Key words: Azomethine; *O*-vanillin; aniline; mild steel; hydrochloric acid; EIS

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Hydrochloric acid (HCl) is used in industries, especially for cleaning and descaling of steel, which leads to higher corrosion current density. However, this issue can be reduced using corrosion inhibitors [1 – 3]. Among several corrosion protection strategies, corrosion inhibitors are more practical in terms of controlling corrosion, especially in an acidic environment, and the approach is also cost-effective [4, 5]. The condensation product of an amine and a ketone or aldehyde, which is known as Schiff base (R_2-C=NR'), is expected to give rise to particularly effective inhibition behavior. Schiff base molecules can enable electron back-donation from the transition metal d-orbitals and eventually stabilize the existing metal-inhibitor bond by the presence of unoccupied π*-orbitals in the molecules [6]. Azomethine has been highlighted as an effective inhibitor based on the ease of synthesis, which mostly requires inexpensive starting materials [4, 7]. A compound that contains atoms such as N, O, and S is known as an active center in adsorption on a metal surface [8, 9]. The organic inhibitor reacts through chemisorption between the adsorbate, which is the acidic environment, and the inhibitor, which interacts with the metal surface through unshared electron pairs or π-electrons in order to form a coordinate type of bond [2].

MATERIALS AND METHODS

1. Materials

The working electrode was a cylindrical disc cut from a Q-Panel mild steel specimen with the dimension of 2 cm × 1 cm × 0.025 cm. The metal disc was coated with epoxy resin with the surface area of 0.05 cm^2. The sample was ground with different grades of silicon carbide abrasive papers, i.e., grades 120, 320, 400, 800, and 1,200, to obtain a bright mirror finish, followed by diamond grade polish to obtain a smooth surface.

2. Preparation and Characterization of Schiff Bases

Schiff bases, as shown in Figure 1, were prepared by condensation with equivalent molar of 5 mmol 2-hydroxy-3-methoxybenzaldehyde with 5 mmol *p*-toluidine and 5 mmol 3-nitroaniline in 10 mL of absolute ethanol. After 3 h of reflux, the products were washed with cold ethanol (3 × 10 mL) to remove excess aldehyde [10].

Anal. Calc. for $C_{15}H_{15}NO_2$ (A3): Yield (%) 60; C, 74.67; H, 6.27; N, 5.81%. Found (%) C, 72.64; H, 6.41; N, 7.71% mp 178-180 ºC; IR (KBr); *v*(C-O) 1258 cm^{-1}, *v*(C=N) 1618 cm^{-1}, *v*(C-H) aromatic 3029 cm^{-1} . ^{1}H-NMR (DMSO, 400 MHz, p.p.m): δ 2.32 (3H, s, Ar-CH_3), δ 3.88 (3H, s, Ar-OCH_3), δ 8.54 (1H, s, HC=N).

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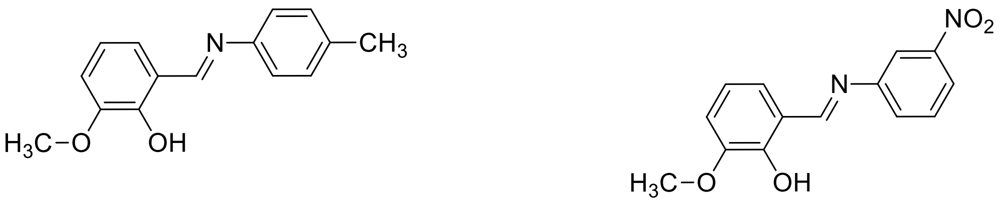


(*Z*)-2-methoxy-6-((p-tolylimino)methyl)phenol (A3)

(*E*)-2-methoxy-6-(((3-nitrophenyl)imino)methyl)phenol (A4)

Figure 1. Molecular structures of A3 and A4

Anal. Calc. for $C_{14}H_{12}N_2O_4$ (A4): Yield (%) 70; C, 61.76; H, 4.44; N, 10.29%. Found (%) C, 62.72; H, 4.97; N, 10.40% mp 179-182 °C; IR (KBr); *v*(C-O) 1253 cm^{-1}, *v*($-NO_2$) 1347, 1523 cm^{-1}, *v*(C=N) 1620 cm^{-1}, *v*(C-H) aromatic 3032 cm^{-1}. ^{1}H-NMR (DMSO, 400 MHz, p.p.m): δ 2.45 (3H, s, Ar-CH_3), δ 3.79 (3H, s, Ar-OCH_3) δ 8.47 (1H, s, HC=N).

3. Electrochemical Measurements

Electrochemical impedance spectroscopy (EIS) and linear polarization measurement (LPR) were performed using a three-electrode system that consisted of mild steel as the working electrode, Ag/AgCl as the reference electrode, and platinum (Pt) wire as the counter electrode. The galvanostatic polarization provided information on corrosion parameters, such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), and Tafel plots (β_a and β_c). The i_{corr} obtained from Tafel extrapolation method was then used to calculate the inhibition efficiency, η_p (%) using the following equation:

$$\eta_p\ (\%) = \frac{i^0_{corr} - i^0_{corr}}{i^0_{corr}} \text{ x } 100$$

Polarization resistance in the presence and absence of an inhibitor is referred to as R_p and R_p^0, respectively. R_p represents resistance, which is affected by different metal-electrolyte interfaces, such as charge transfer resistance. The resistance occurs due to adsorbed corrosion products and inhibitors. The inhibition efficiency, η_z (%) is defined as:

$$\eta_z\ (\%) = \frac{R_p - R_p^0}{R_p} \text{ x } 100$$

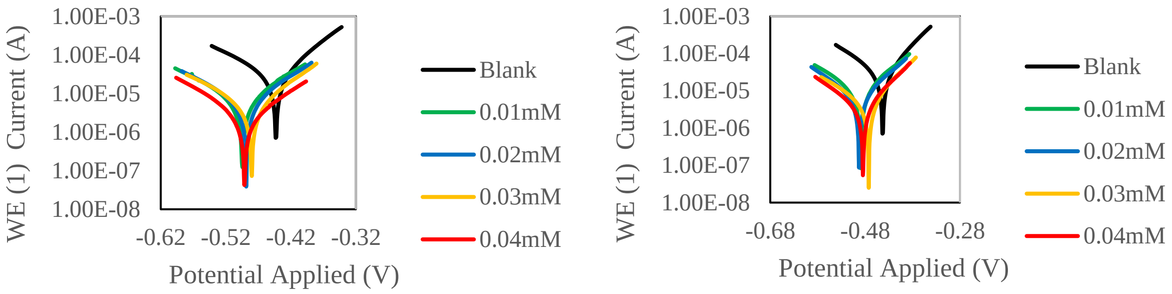
RESULTS AND DISCUSSION

1. Polarization Measurements

Figure 2 shows the potentiodynamic polarization curve of mild steel in 1 M HCl in the absence and presence of inhibitors A3 and A4 at various concentrations (0.01, 0.02, 0.03, and 0.04 mM). The evaluation of the cathodic and anodic Tafel slopes (β_a and β_c, respectively), and i_{corr} was conducted using Tafel extrapolation of the current-potential lines at the corresponding E_{corr}, as shown in Table 1. The cathodic and anodic polarization curves obtained at different concentrations are shown in Figure 2.

Table 1. Polarization parameters for mild steel in 1 M HCl as blank and inhibitors A3 and A4 obtained at different concentrations

Sample	Conc.(mM)	$-E_{corr}$ (mV)	β_a (mV/dec)	β_c (mV/dec)	*I*corr (μA/cm^2)	%IE
Blank	0	443	124	78	570	0
A3	0.01	495	124	102	140	75
	0.02	488	128	100	130	77
	0.03	480	118	91	95	83
	0.04	491	100	111	53	91
A4	0.01	490	146	105	221	61
	0.02	493	142	103	162	72
	0.03	472	151	78	99	83
	0.04	484	151	92	89	84



(a) A3

b) A4

Figure 2. The variation of different potential applied and current change for mild steel corrosion in the presence and absence of inhibitors

It was observed that the inhibition efficiency of A3 (91%) was higher than A4 (84%). This indicated that the presence of electron donating group ($-CH_3$) substituent in the aniline enhanced the inhibition efficiency of the compound. Inhibitors A3 and A4 retarded both of the oxidation of iron ($Fe \rightarrow Fe^{2+} + 2e^-$) and reduction reaction, yielding hydrogen gas ($2H^+ + 2e^- \rightarrow H_2$). The presence of both inhibitors shifted the corrosion potential (E_{corr}) towards the negative direction, which indicated that both inhibitors acted as anodic inhibitors. If the corrosion potential shift exceeds ±85 mV with respect to corrosion potential of uninhibited solution, only then the inhibitor can be considered as an anodic or cathodic type of inhibitor [11], [12]. In this study, it was found that the corrosion potential shifted less than ±85 mV, which indicated that inhibitors A3 and A4 could be considered as mixed type inhibitors.

2. Electrochemical Impedance Measurement

EIS technique was used to test the inhibition efficiency of A3 and A4. The electrochemical parameters for both A3 and A4 on mild steel in 1 M HCl are tabulated in Table 2. Based on Table 2, A3 gave 87% inhibition efficiency, which was similar to A4. The current density of mild steel (i_{corr}) for A3 and A4 was lower than the blank sample **(Table 1)**.

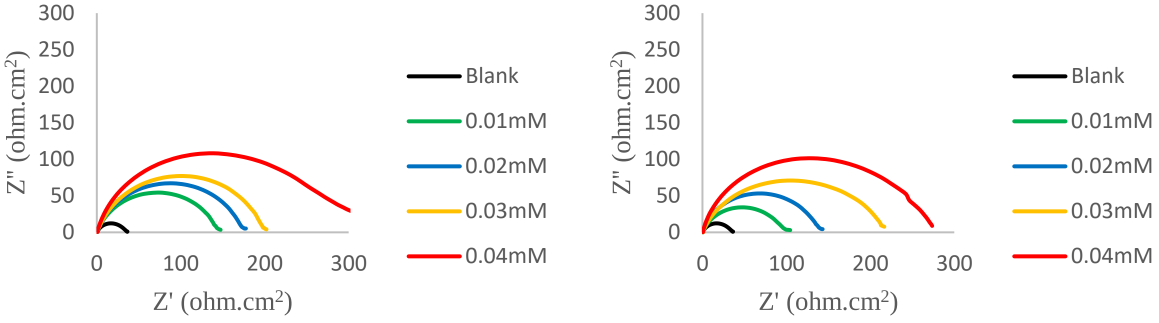
Figure 3 shows the impedance spectra in Nyquist format for mild steel in both A3 and A4 with 1 M HCl as the blank sample. The impedance diagram shown on Figure 3 displayed one single capacitive loop that formed a semi-circle for both studied compound. The capacitive loop indicated that the corrosion of mild steel in 1 M HCl solution was mainly controlled by the charge transfer process and the formation of a protective layer on the metal surface [7]. Both Nyquist plots gave a depressed semi-circle, which suggested that both solution did follow the ideal capacitance due to the dispersing effect from the surface roughness of mild steel [13].

3. Scanning Electron Microscopy Analysis

The surface morphology of mild steel after immersion in 1 M HCl in the absence and presence of inhibitors was initially evaluated using scanning electron microscopy (SEM) analysis. Figure 4(a) shows the mild steel surface in 1 M HCl whereas

Table 2. Impedance parameters for mild steel with A3 and A4 as inhibitors obtained at different concentrations

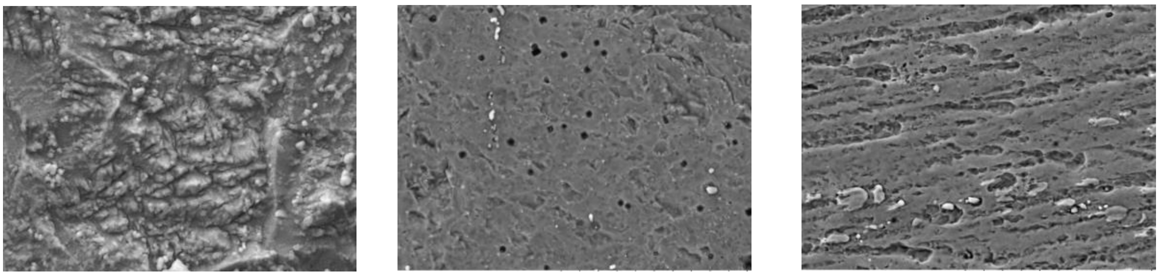
Sample	Conc. (mM)	R_{ct} (Ω cm^2)	C_{dl} (μf cm^{-2})	IE (%)
Blank	0	34	43	0
A3	0.01	122	81	75
	0.02	148	78	79
	0.03	169	74	82
	0.04	243	68	87
A4	0.01	81	108	62
	0.02	120	81	74
	0.03	162	77	81
	0.04	230	60	87



(a) A3

(b) A4

Figure 3. The Nyquist plots for mild steel corrosion in the presence and absence of A3 and A4



a) Blank

b) A3

c) A4

Figure 4. SEM images of mild steel surfaces in (a) 1 M HCl, (b) 1 M HCl and 0.04 mM of A3, and (c) 1 M HCl and 0.04 mM of A4

Figures 4(b) and (c) show the mild steel surface in 1 M HCl containing 0.04 mM of A3 and A4, respectively. The mild steel immersed in 1 M HCl solution showed a rougher and eroded surface that completely corroded. The presence of inhibitors reduced the corrosive attack from the acidic solution, thus resulted in less deterioration on the mild steel surface.

4. Atomic Force Microscopy Analysis

The two-dimensional (2D) and three-dimensional (3D) atomic force microscopy (AFM) images of a mild steel surface after exposure to 1 M HCl solution for 24 h are shown in Figure 5(a). From the figure, the mild steel surface exposed to a corrosive solution has a considerably porous structure. The roughness of the surface was 152.8 nm. However, mild steel surfaces were smoother in the presence of 0.04 mM A3 and 0.04 mM A4, as shown in Figures 5(b) and (c), respectively. This was due to the presence of inhibitors on the mild steel surfaces that reduced the corrosion rate of mild steel. The surface roughness values for mild steel after the addition of A3 and A4 were 37.49 and 98 nm, respectively.

CONCLUSION

Ligands derived from 2-hydroxy-3-methoxy-benzaldehyde and aniline derivatives were successfully synthesized through condensation and achieved high yields. Both ligands, namely A3 and A4, were efficient inhibitors for mild steel in 1 M HCl. Based on this research, it shows that the presence of azomethine inhibitors will improve the inhibition efficiency on mild steel surface as mixed-type inhibitors. Based on SEM and AFM results, it was confirmed that the inhibitors effectively act as protective layers by improving the mild steel surfaces compared to the untreated sample.

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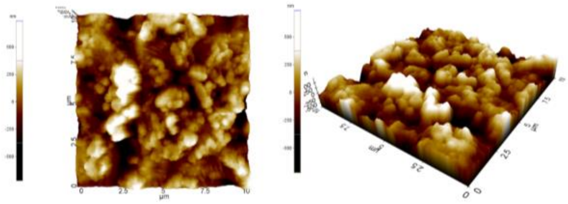
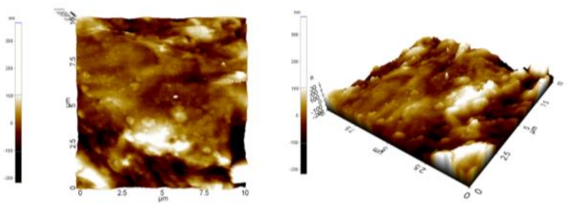
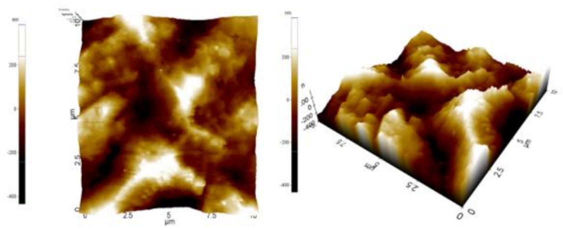


a) Blank



b) A3



c) A4

Figure 5. 2D and 3D AFM images for mild steel immersed in (a) 1 M HCl solution and in the presence of (b) 0.04 mM of A3 and (c) 0.04 mM of A4

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