Effect of the combined admixture of 4-methyl-norvalin and 2-Methoxy-4-formylphenol on the corrosion inhibition of low carbon steel in artificial seawater solution

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Abstract. The synergistic effect of 4-methyl-norvalin and 2-methoxy-4-formylphenol on the corrosion inhibition of low carbon steel in artificial seawater (3.5 wt.% NaCl solution) was studied with potentiodynamic polarization technique, open circuit potential measurement and optical microscopic analysis. Results obtained from the electrochemical test showed the organic derivatives performed effectively with optimal inhibition performance of 89%. Mixed type inhibition behavior was observed. Anodic corrosion potential shift occurred because of effective surface coverage of the inhibitor molecules. The adsorption mode was determined to occur through physisorption reaction from thermodynamic calculations in agreement with the Langmuir, Frumkin and Freundlich isotherms at correlation coefficients beyond 0.7. Corroded morphology of steel occurred without with inhibitor compared to the steel from solution at highest inhibitor concentration.

1. Introduction
The corrosion process results in deterioration of the surface properties and metallic substrate of carbon steels. Despite the weak resistance of carbon steel to corrosion, it has extensive industrial application across most industries. Marine environments have abundance of chloride anions hence the serious debilitating effect of corrosion encountered metal alloys in such environments. Corrosion prevention by chemical compounds known as inhibitors has been proven to be one of the most feasible, reliable and cost-effective methods [1]. Previous individual research on the corrosion inhibition effect of 4-methyl-norvalin and 2-methoxy-4-formylphenol compounds have been done in acid solution with above average results [2-6]. The purpose of this study is to assess the adsorption and corrosion inhibition performance of 4-methyl-norvalin and 2-methoxy-4-formylphenol admixture on low carbon steel in artificial seawater solution.

2. Experimental methods
Low carbon steel (LCS) with cylindrical configuration (diameter of 1.2 cm²) has nominal (wt. %) composition shown in Table 1. The steel was machined and underwent metallographic preparation before washing with deionized H₂O and methyl-ketone. 4-methyl-norvalin with molecular formular C₆H₁₃NO₂ and molar mass of 131.17 g/mol, and 2-Methoxy-4-formylphenol with a molecular formular C₈H₈O₃ and molar mass of 152.15 g/mol were evaluated in the admixed form for corrosion inhibition. The compounds (4MMP) were prepared in combined molar concentrations of 1.76 x 10⁻², 3.53 x 10⁻², 5.29 x 10⁻², 7.06 x 10⁻², 8.82 x 10⁻², 1.06 x 10⁻¹ per 200 mL of 3.5% NaCl solution. Potentiodynamic polarization analysis was performed at 35 °C with a triple electrode system Graphs were produced at a scan rate of 0.0015 V/s between potentials of -1.25 V and +1.5 V. Optical images of corroded and 4MMP inhibited LCS morphology were studied after electrochemical analysis with...
Omax trinocular metallurgical microscope. Open circuit potential measurement (OCP) was performed at 0.05 V/s step potential for 3000s to study the active-passive behavior of LCS.

### Table 1. Composition (wt. %) of Low carbon steel

| Element | C    | Si   | Mn  | P    | S    | Cu   | Ni   | Al   | Fe   |
|---------|------|------|-----|------|------|------|------|------|------|
| % Composition | 0.401 | 0.169 | 0.440 | 0.005 | 0.012 | 0.080 | 0.008 | 0.025 | 98.86 |

#### 3. Result and discussion

#### 3.1 Potentiodynamic polarization

The potentiodynamic polarization plots indicating the anodic-cathodic behavior of LCS in 4MMP /3.5%NaCl solution is shown in Fig. 1., Table 2 depicts the data obtained. LCS at 0% and 0.5% 4MMP severely deteriorated in the presence of Cl⁻ ions attaining corrosion rate values of 2 mm/y and 1.99 mm/y. 4MMP at 0.5% was unable to inhibit the corrosion of LCS due to insufficient protonated molecules to oppose the deterioration effect of Cl⁻ ions. At 1% - 2% 4MMP, the corrosion rate decreased to values between 0.96 mm/y and 0.75 mm/y corresponding to inhibition efficiencies of 51.84%, 55.45% and 62.73% respectively due to the availability of enough 4MMP molecules to inhibit the electrochemical action of chlorides. While changes in the cathodic Tafel slope a marginal a significant decrease in anodic Tafel slope was observed beyond 0.5% 4MMP due to decrease in anodic reactions on the steel. Observation of the polarization plot shows the cathodic branches of the plot with respect to 4MMP concentration are quite similar indicating the cathodic reaction mechanism is under activation control. The anodic branch of the polarization plot at 0% 4MMP and 0.5% 4MMP were linear due to oxidation reaction on LCS surface, however beyond 0.5% 4MMP short passivation behavior was observed due to inhibiting action of 4MMP compound. It shows the inhibition mechanism is through surface coverage. At 2.5% 4MMP and 2% 4MMP, the inhibition efficiency has attained values of 80.85% and 89% respectively signifying effective inhibition of LCS corrosion. The maximum change in corrosion potential of LCS between 0% 4MMP and 1% 4MMP in the reduction reaction direction is 81 mV thus it is a mixed type inhibitor [7].

![Figure 1. LCS corrosion polarization plots from 3.5% NaCl/0% - 2.5% 4MMP](image)

### Table 2. Results of potentiodynamic polarization test of LCS corrosion in 3.5% NaCl/0% - 2.5% 4MMP

| Sample | 4MMP Conc. (%) | 4MMP Conc. (M) | LCS C_e (mm/y) | 4MMP Y, (%) | C_A (A/cm²) | C_d (V) | R_p (Ω) | R_g (V/dec) |
|--------|----------------|----------------|----------------|-------------|-------------|--------|--------|-------------|
| A      | 0              | 0              | 2.00           | 0.00        | 1.95E-04    | 1.73E-04| -0.593 | 116.00      |
| B      | 0.5            | 1.76E-2       | 1.99           | 0.73        | 1.93E-04    | 1.71E-04| -0.604 | 106.00      |
| C      | 1              | 3.53E-2       | 0.96           | 51.84       | 9.3E-05     | 8.68E-05| -0.674 | 273.80      |
| D      | 1.5            | 5.29E-2       | 0.89           | 55.45       | 8.68E-05    | 7.68E-05| -0.659 | 296.06      |
| E      | 2              | 7.06E-2       | 0.75           | 62.73       | 7.22E-05    | 6.42E-05| -0.654 | 353.50      |
| F      | 2.5            | 8.82E-2       | 0.38           | 80.85       | 3.73E-05    | 3.30E-05| -0.586 | 688.90      |
| G      | 3              | 1.06E-1       | 0.22           | 89.00       | 2.49E-05    | 1.90E-05| -0.651 | 739.70      |
3.2 Inhibition Mechanism of 4MMP
4MMP consisting of 4-methyl-norvalin and 2-Methoxy-4-formylphenol are compounds consisting of organic molecules which adsors on the metallic surface during corrosion inhibition reactions inhibiting the diffusion and electrochemical action of corrosive species. These compounds form precipitates with metal cations on the ionized metal surface [8]. Observation of the inhibition reaction mechanism in the presence of 4MMP shows passivation resulting from film formation (surface coverage) of protonated 4MMP molecules occurred on LCS surface as evident on the anodic branch of the polarization plots.

3.3 Open circuit potential measurement (OCP)
The OCP plot of LCS in 3.5% NaCl/0%, 0.5% and 3% 4MMP versus exposure time is shown in Fig. 2. The OCP value of LCS (3.5% NaCl/0% 4MMP) at 26.45 s is the most electronegative (-0.680 V) due to surface oxidation reactions. The value later progressed sharply at short time interval to -0.503 V at 200 s due to short instantaneous passivation. However, the oxide formed are porous in nature, as a result the OCP immediately decreased to -0.551 V at 500 s before remaining marginally stable till 750.01 s (-0.554 V). Beyond this point the OCP values of LCS at 3.5% NaCl/0% 4MMP continue to decrease till 3200 s. The presence of 4MMP at 0.5% concentration caused an instantaneous increase in OCP due to marginal passivation of LCS 250 s at -0.559 V, beyond which the OCP value remained thermodynamically stable and at higher OCP values than LCS at 0% 4MMP. At 3% 4MMP the OCP value of LCS starting at -0.605 V (0 s) increased to -0.460 V at 300 s due to the corrosion inhibiting action of 4MMP. A progressive but stable marginal decrease later occurred till the end of the OCP test.

![Figure 2. Variation of LCS OCP values versus exposure time in 3.5% NaCl/4MMP compound](image)

3.4 Adsorption isotherm studies
Langmuir, Frumkin and Freundlich isotherm models produced significantly high correlation coefficients amongst other isotherms evaluated to further understand the nature of 4MMP adsorption and corrosion inhibition of LCS [9]. Fig. 3 shows the graphical illustration of $\frac{C_{\text{4MMP}}}{\theta}$ vs $C_{\text{4MMP}}$ at correlation coefficient of 0.8024 with respect to Langmuir equation below.

$$\theta = \frac{K_{\text{4MMP}}C_{\text{4MMP}}}{1+K_{\text{4MMP}}C_{\text{4MMP}}^c}$$  \hspace{1cm} (1)

$\theta$ is the sum of 4MMP adsorbed per unit gram on LCS surface at constant temperature. $C_{\text{4MMP}}$ is 4MMP concentration and $K_{\text{4MMP}}$ is the equilibrium constant of adsorption. Fig. 4(a) shows the Frumkin isotherm graph of graph of log[$\theta/(1-\theta)$] against $\theta$ with correlation coefficient of 0.9813 according to equation 2.
\[ \frac{\theta}{1 - \theta} = K Ce^{2a\theta}, \quad (2) \]

\( \alpha \) is the lateral synergism parameter determined from the gradient of the graphical illustration of the Frumkin isotherm and \( K \) is the adsorption-desorption constant. Fig. 4(b) shows the Freundlich isotherm graph for 4MMP adhesion and assimilation with correlation coefficient of 0.7570 according to equation 3 and 4.

\[ \theta = KC^n \quad (3) \]

\[ \log \theta = n \log C + \log K_{ads} \quad (4) \]

\( n \) is a constant subject to the properties of the inhibitor molecules involved in the adsorption reaction. \( K_{ads} \) is the adsorption-desorption equilibrium constant showing the adsorption strength.

\[ y = 0.7945x + 5E-05 \quad R^2 = 0.8024 \]

Fig. 3. Langmuir isotherm plot of \( \frac{C_{4MMP}}{\theta} \) versus 4MMP concentration

\[ y = 1.1725x - 0.5866 \quad R^2 = 0.9813 \]

\[ y = 18.75x + 77.547 \quad R^2 = 0.7570 \]

Fig. 4. (a) Graph of Frumkin isotherm, \( \log \left[ \frac{\theta}{(1 - \theta)C} \right] \) versus \( \theta \) and (b) Graph of Freundlich isotherm, \( \log 4MMP \) concentration vs \( \log \) surface coverage.

### 3.5 Thermodynamics of inhibitor adsorption

Gibbs free energy data values are shown in Table 3. The highest \( \Delta G_{ads}^{o} \) value obtained is \(-20.70 \text{ KJmol}^{-1}\) while the lowest significant \( \Delta G_{ads}^{o} \) value obtained is \(-18.42 \text{ KJmol}^{-1}\). The \( \Delta G_{ads}^{o} \) values shows the mechanism of adsorption is through physical attraction which shows that surface coverage of the inhibiting compound hinders the movement of the corrosive anions [10].
Table 3. Gibbs free energy ($\Delta G^o_{ads}$), surface coverage ($\theta$) and equilibrium constant of adsorption ($K_{ads}$) data for 4MMP adsorption on LCS

| Sample | 4MMP Concentration (M) | Surface Coverage ($\theta$) | Equilibrium Constant of adsorption ($K$) | Gibbs Free Energy, $\Delta G$ (KJmol$^{-1}$) |
|--------|------------------------|----------------------------|----------------------------------------|------------------------------------------|
| A      | 0                      | 0                          | 0                                      | 0                                        |
| B      | 1.76E-02               | 0.007                      | 0.42                                   | -7.79                                    |
| C      | 3.53E-02               | 0.518                      | 30.49                                  | -18.42                                   |
| D      | 5.29E-02               | 0.555                      | 23.53                                  | -17.78                                   |
| E      | 7.06E-02               | 0.627                      | 23.84                                  | -17.81                                   |
| F      | 8.82E-02               | 0.809                      | 47.87                                  | -19.54                                   |
| G      | 1.06E-01               | 0.890                      | 76.33                                  | -20.70                                   |

3.6 Morphological studies

Fig. 5(a) to 5(b) shows the optical images of LCS before corrosion, and after corrosion in 3.5% NaCl/0%, 0.5% and 3% 4MMP solution. The image in Fig. 6(b) differs from Fig 6(a) due to the destructive effect of Cl$^-\text{anions.}$ Corrosion pits coupled with general surface deterioration are visible with corrosion products of iron oxides. Addition of 4MMP at 0.5% concentration [Fig. 6(a)] did not offer any significant protection. General corrosion seems to have been inhibited however the corrosion pits on the surface appears larger. The LCS morphology at 3% 4MMP [Fig. 6(b)] shows a remarkable improvement in comparison the earlier observed surfaces.

Figure 5. Optical images of LCS at mag. x40 and x100 (a) LCS morphology before corrosion, (b) LCS morphology after corrosion in 3.5% NaCl

Figure 6. Optical images of LCS at mag. x40 and x100 (a) LCS morphology after corrosion in 3.5% NaCl/0.5% 4MMP, (b) LCS morphology after corrosion in 3.5% NaCl/3% 4MMP

4. Conclusion

4-methyl-norvalin and 2-Methoxy-4-formylphenol synergistically suppressed the electrochemical action of chlorides on the carbon steel surface in artificial seawater. Inhibition efficiency performance of the compounds was well above 80%. The mechanism of inhibition was determined to be through surface coverage. This caused a large anodic shift in Corrosion potential shifted anodically in the presence of the compound. Physisorption adsorption dominated the mechanism of inhibitor-metal interaction.
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