Study of the synergistic effect of 2-methoxy-4-formylphenol and sodium molybdenum oxide on the corrosion inhibition of 3CR12 ferritic steel in dilute sulphuric acid

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The synergistic effect of the corrosion inhibition properties of 2-methoxy-4-formylphenol and sodium molybdenum oxide on the electrochemical property of 3CR12 ferritic stainless steel in 2M H2SO4 acid solution was assessed through coupon analysis, potentiodynamic polarization technique, IR spectroscopy and micro-analytical technique. Experimental data showed the combined admixture effectively inhibited the steel corrosion at the concentrations analyzed with a maximum inhibition efficiency of 94.47% and 89.71% from coupon analysis and potentiodynamic polarization due to the electrochemical action and inhibition of the steel by the ionized molecules of the inhibiting compound which influenced the mechanism of the redox reactions responsible to corrosion and surface deterioration. Results from corrosion thermodynamic calculations showed chemisorption adsorption mechanism. Infrared spectroscopic images exposed the functional groups of the molecules involved for the corrosion inhibition reaction. Micro-analytical images showed sharp contrast in surface morphology between the inhibited and corroded test specimens under study. Cracks, intergranular and pitting corrosion in addition to severe surface deterioration was observed in the uninhibited samples. Inhibitor adsorption fits the Langmuir isotherm model.

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Introduction

Stainless steels are extensively applied industrially such as in desalination plants, petrochemical, construction, chemical processing, pharmaceutical, power generating plant, industrial cleaning, oil well acidizing and pickling process etc. because of their inherent stability, stable corrosion resistance and good mechanical properties. The excellent corrosion resistance is primarily as a result of the chemically produced oxide film which formed on its surface when exposed to an electrolyte. The film is the product of chemical interaction between iron substrate metal, chromium oxides formed and hydroxides at the metal-film interface [1]. The strength of the passive film is a product of the environment with which the stainless is exposed to and the alloy content. Corrosion deterioration of stainless steels is a major industrial problem with numerous investigators working to assess and control it. Most steels tends to be unstable in some conditions due to their inherent characteristics, reacting with the environments, forming a chemical compound in a more stable and lower energy state [2]. Damage due to corrosion is responsible for fluid leakages, structural weakness and eventual failure of stainless steels. This is responsible for the high cost for inspection/monitoring, repair/replacement and high cost of industrial end product, thus the need for cost effective corrosion control and inhibition measures [3]. 3CR12 ferritic stainless steel is the utility steel with the exceptional property high temperature and corrosion resistance as in other steel products coupled with their weldability and formability. The steel is low priced with significant chromium content produced from the modification of grade 409 steel. It is resistant to mild corrosion and wet abrasion from strong acids and alkalis, and cracking resulted from chloride stress corrosion. The steel is employed in applications where aluminum, galvanized and carbon steels underperform, however, its drawback is low resistance to crevice and pitting corrosion in chloride containing solutions.

One of the most cost proven and reliable means of preventing corrosion is through the consistent application of corrosion inhibitors. Inhibitors are generally applied to significantly reduce corrosion degradation on stainless steels. Chemicals of organic origin and constituents have been proven to be very effective corrosion inhibiting agents for a wide variety of steels in acidic medium. Use of organic compounds for corrosion inhibition has been

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Acid test solution

4.189 M acid solutions were prepared using analytical grade acid (98%) with deionized water.

Molecular properties of MPSB inhibiting compound.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Compound</th>
<th>Molecular Formula</th>
<th>Molar Mass (gmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sodium molybdenum oxide</td>
<td>Na₂MoO₄</td>
<td>241.95</td>
</tr>
<tr>
<td>2</td>
<td>2-Methoxy-4-formylphenol</td>
<td>C₈H₈O₃</td>
<td>152.15</td>
</tr>
</tbody>
</table>

Sample preparation of ferritic stainless steels

The FSS and HCS samples were machined into seven (7) test pieces with mean length of 0.7 mm. The samples were further prepared metallographically using silicon carbide grit papers of 80, 300, 600 and 1000 grits before polishing to 6 μm with Pen Struers diamond paste. Each sample was cleaned with deionized water and propanone, and placed in a desiccator for coupon analysis and potentiodynamic polarization test according to ASTM G1-03(2011).

Coupon measurement

Ferritic steel coupons were measured before separate immersion in 200 mL of the corrosion test media for 240 h at of 30 °C. The samples were taking out separately from the electrolyte at 24 h meantime, cleansed with deionized water and propanone, dried and measured again according to ASTM G31-72(2004). Plots of corrosion rate values, υ (mm/y) and MPSB inhibition efficiency, η (%) against measured time T were outlined from the results obtained during the corrosion test period. Corrosion rate (υ) is determined as follows [20].

\[
υ = \frac{87.6ω}{DAT}
\]  

where ω is the mass loss in mg, D is the density in g/cm³, A is the total surface area of the coupon in cm² and 87.6 is a constant. Inhibition efficiency (η) was determined from the expression below:

\[
η = \left(\frac{ω₁ - ω₂}{ω₁}\right) \times 100
\]

where ω₁ and ω₂ are the mass loss at predetermined concentrations of MPSB. η was determined at the MPSB concentrations studied during the evaluation period. Surface coverage was evaluated from the expression [21,22]:

\[
θ = \left[1 - \frac{ω₂}{ω₁}\right]
\]

Table 1

Elemental composition of FSS.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (%)</td>
<td>0.050</td>
<td>0.182</td>
<td>1.830</td>
<td>0.12</td>
<td>0.017</td>
<td>0.102</td>
<td>1.3</td>
<td>13</td>
<td>82.80</td>
</tr>
</tbody>
</table>

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where $\theta$ is the degree of MPSB compound, adsorbed per gram of the steel samples. $\omega_1$ and $\omega_2$ are the mass loss of each steel coupon at predetermined concentrations of MPSB in the acid media.

**Potentiodynamic polarization technique**

The polarization test was achieved with the cylindrical ferritic steel electrodes encased in acrylic resin mounts with exposed surface area of 254 and 132.7 mm². The electrodes were prepared with respect to ASTM G59-97(2014). Electrochemical studies were conducted at 30 °C using Digi-Ivy 2300 potentiostat and glass cell containing 200 ml of the corrosive test solution at predetermined concentrations of MPSB. Platinum rod was used as the counter electrode and silver chloride electrode (Ag/AgCl) as the reference electrode. Measurement was done from −1.5 V to +1.5 V at a scan rate of 0.0015 V/s according to ASTM G102-89(2015). Corrosion current density ($j_{cr}$) and corrosion potential ($E_{cr}$) were calculated from the Tafel outline of potential (V) versus current (log), (A cm²). The corrosion rate ($\nu$) and the inhibition efficiency ($\eta_2$) % were evaluated from the expression below.

\[ y = \frac{0.00327 \times j_{cor} \times E_q}{D} \]

$j_{cr}$ is the current density in $\mu$A/cm², $D$ is the density in g/cm³, $E_q$ is the sample equivalent weight in grams. 0.00327 is a constant for polarization results for FSS in 2M H$_2$SO$_4$ at 0%–1.5% MPSB.

**Infrared spectroscopy**

The MPSB compound in H$_2$SO$_4$ acid was exposed to specific range of infrared ray beams. The transmittance and reflectance of the infrared beams at various frequencies were decoded and transformed into an IR absorption plot consisting of spectra peaks. The spectral pattern was evaluated and equated according to IR absorption table to identify the functional groups involved in the corrosion inhibition reactions.

**Result and discussion**

**Potentiodynamic polarization studies**

Table 3 shows the data for influence of MPSB inhibitor on the corrosion polarization behaviour of FSS in 2M H$_2$SO$_4$. Fig. 2 shows the polarization plot obtained. Observation of Table 3 depicts the significant variation in corrosion rate and polarization resistance values for FSS samples at 0.25%–1.5% MPSB concentration in comparison to FSS sample at 0% MPSB. The corrosion rates for the inhibited FSS samples decreased consistently till 1.5% MPSB. This observation corresponds with the values obtained for polarization resistance (Table 3). At 0.25% MPSB the inhibition efficiency is at the lowest (81.13%) but increases with increase in MPSB concentration to 89.71% at 1.5% MPSB. The results show that MPSB
effectively inhibits the corrosion of FSS in H₂SO₄ at the concentrations studied. The corrosion current also decreased significantly with increment in concentration of MPSB. The inhibition efficiency of MPSB is dependent to a minimal degree on the values of its concentration in the acid media. This is due to the presence of an effective MPSB film which prevents corrosion by limiting the diffusion of sulphate anions (SO₄²⁻) to the metal surface, as well as inhibiting the electrolytic transport of metallic cations. It is also suggested that MPSB modifies the corrosive environment, significantly weakening the oxidizing strength of the corrosive media [25,26].

The anodic/cathodic polarization plots in Fig. 2 shows active and anodic-passivation polarization behavior with and without MPSB compound. The plot for 0% MPSB shows corrosion potential of −0.376 V which corresponds to values of active corrosion reactions and deterioration of the FSS. The polarization plots for FSS samples with varying degree of MPSB concentration occurred at corrosion potentials (−0.313V−0.283 V) which correspond to passivation potentials. Even though similar electrochemical behavior was observed, the corrosion potential shifts entirely towards anodic values suggesting that the inhibition mechanism is probably through suppression of the anodic oxidation reactions responsible for FSS dissolution (Fe → Fe²⁺ + 2e⁻) [27]. This phenomenon is further supported from results obtained for polarization resistance on Table 3 where the values increased from 36.39 Ω to 45.99 Ω. The molybdate ion is an anodic corrosion inhibitor and the synergistic effect of 2-methoxy-4-formylphenol component of MPSB does not change its inhibition property [17]. Previous research has shown that the 2-methoxy-4-formylphenol component of MPSB is a mixed type inhibitor with strong influence on cathodic reactions. Its physicochemical characteristics are due to the composition of its functional groups (aldehyde, hydroxyl, and ether) and their electrochemical property [28]. This property is through the charge of the carbonyl group and the astringency of any α-hydrogen within their structure. The hydroxyl groups within the compound are polarized in the electrolyte to enable the O₂ atom release electron. The hydroxyl group causes electrostatic attraction with the metal [29]. The compound accumulates a passive hydrophobic covering of inhibitor molecules adsorbed onto the alloy, which prevents the dissolution of the metal within the aqueous solution.

The precipitation Fe²⁺-MPSB on the anodic area of the steel controls the anodic reaction. The reduction reaction is under the influence of Zn(OH)₂ formation on the cathodic areas of the metal surface. The anodic and cathodic Tafel slopes were slightly influenced by changes in MPSB concentration suggesting that changes to the redox reactions relating to the mechanism of inhibition is through decrease in the surface area of FSS for corrosion process [30]. The optimal change in corrosion potential in H₂SO₄ is 123 mV in the anodic direction, thus MPSB is an anodic type inhibitor [29,31]. The molybdate ion component of MPSB has a higher radius than the sulfate anion, thus a higher specific adsorption [32]. It absorbs onto the steel surface and is reduced (Mo⁶⁺ reduces to Mo⁴⁺, MoO₂ is formed) according to the reaction in Eq. (6) [14]. The reaction of H⁺ with O²⁻ simultaneously results in the dilution of local solution acidity causing a less oxidizing solution. The molybdate ion scavenges the dissolved oxygen, stifles the anode reaction and supports the passivation of the metal surface.

\[
\text{MoO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{MoO}_2 + 2\text{H}_2\text{O} \quad (6)
\]

**Coupon measurements**

Calculated results obtained for weight loss (g), corrosion rate (μm/yr) and percentage inhibition efficiency (n) for the interaction of MPSB inhibiting compound on FSS in H₂SO₄ solutions are presented in Table 4. Figs. 3 and 4 show the plot of corrosion rate and MPSB inhibition efficiency versus exposure time in the acid media. MPSB had a strongly influenced the reduction-oxidation corrosion reactions responsible for FSS degradation. MPSB being an anodic inhibitor as discussed previously, its inhibition mode is through adsorption whereby it precipitates on the reactive sites of the steel surface. The release of FSS cations into the acid solution through the electrochemical action of sulphate ions was significantly minimized. Observation of Table 4 and Fig. 3 show the significant variation in corrosion rate values between the uninhibited FSS sample and samples inhibited by MPSB similar in trend to observation from potentiodynamic polarization test. The corrosion rate for FSS at 0% MPSB concentration decreases steadily.

**Table 4**

<table>
<thead>
<tr>
<th>FSS Samples</th>
<th>Weight Loss (g)</th>
<th>Corrosion Rate (μm/yr)</th>
<th>MPSB Inhibition Efficiency (%)</th>
<th>MPSB Concentration (%)</th>
<th>MPSB Concentration (Molarity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>11.264</td>
<td>0.060</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>1.617</td>
<td>0.009</td>
<td>85.65</td>
<td>0.13</td>
<td>6.9819E–06</td>
</tr>
<tr>
<td>C</td>
<td>1.479</td>
<td>0.008</td>
<td>86.87</td>
<td>0.25</td>
<td>1.3964E–05</td>
</tr>
<tr>
<td>D</td>
<td>2.165</td>
<td>0.012</td>
<td>80.78</td>
<td>0.38</td>
<td>2.0946E–05</td>
</tr>
<tr>
<td>E</td>
<td>0.711</td>
<td>0.004</td>
<td>93.68</td>
<td>0.50</td>
<td>2.7928E–05</td>
</tr>
<tr>
<td>F</td>
<td>0.367</td>
<td>0.002</td>
<td>96.74</td>
<td>0.63</td>
<td>3.4909E–05</td>
</tr>
<tr>
<td>G</td>
<td>0.623</td>
<td>0.003</td>
<td>94.47</td>
<td>0.75</td>
<td>4.1891E–05</td>
</tr>
</tbody>
</table>

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MPSB studies of the adsorption characteristics of MPSB compound were influence the mechanism and type of adsorption [36]. Further of ionic adsorption and the electrochemical potential strongly metallic surface charge/properties, electronic properties, degree lar/electrostatic forces at the interface. The ionization potential, the metal ion/solution interface and is subject to the intermolecu- Adsorption of MPSB ionized molecules on FSS surface occurs at insoluble protective barrier of ferric molybdate[35]. of dissolved oxygen to give insoluble ferric (Fe+3) ions which forms (Fe+2) ions. The complex though unstable, oxidizes in the presence on the surface of the steel and form a complex with the ferrous [34]. The molybdate ions of sodium molybdenum oxide adsorb preventing the oxidation reaction of corrosive ions with the steel film adsorbs through chemical reaction mechanism onto the steel Thermodynamics of the corrosion inhibition mechanism

Results of Gibbs free energy (ΔG_ads) for MPSB adsorption on FSS (Table 5) was evaluated from Eq. (8).

\[
\Delta G_{ads} = -2.303RT \log [55.5K_{ads}] 
\]  

(8)

where 55.5 is the molar concentration of water in the solution, R is the universal gas constant, T is the absolute temperature and K_{ads} is the equilibrium constant of adsorption for MPSB. K_{ads} is related to surface coverage (θ) from Eq. (8). The heterogeneous characteristics of FSS morphology cause the changes in ΔG_{ads} of adsorption for MPSB with changes in surface

![Fig. 4. Plot of inhibition versus exposure time for 3CR12 ferritic steel in 2M H_2SO_4 at 0–1.5%MPSB.](image-url)

![Fig. 5. Plot of θ versus MPSB concentration (C) in 2M H_2SO_4.](image-url)

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360 coverage values [39–41]. This relationship is responsible for the
361 differences in adsorption energies presented in the Table 5. The
362 negative values of $D^\text{Go}_{\text{ads}}$ show the adsorption mechanism is spon-
363 taneous [42]. Values of $D^\text{Go}_{\text{ads}}$ around $/C040 \text{kJmol}^{-1}$ depict
364 chemisorption adsorption reactions. Reactions at this value involve
365 charge sharing or transfer between the inhibitor cations and the
366 valence electrons of the steel forming a co-ordinate covalent bond.
367 The highest $D^\text{Go}_{\text{ads}}$ value in H$_2$SO$_4$ is $/C043.80 \text{kJ mol}^{-1}$ at 0.25%
368 MPSB while the lowest is $/C041.96 \text{kJ mol}^{-1}$ at 1% MPSB.

369 **IR spectroscopy**

The IR spectra of 2M H$_2$SO$_4$/MPSB solution before and after the
corrosion tests are shown in Fig. 6. Observation of the spectra
peaks shows that the test solution had almost similar peaks; how-
ever, the intensities decreased/increased at some spectra peaks
after the corrosion test due to the reaction of MPSB with FSS and
acid to form chemical complexes. The spectra peaks of 3343.52,
1635.63, 1182.28, 1047.14 and 873.14 cm$^{-1}$ before the corro-
sion test generally corresponds to O–H stretch, H–bonded (alco-
hols, phenols), N–H stretch (primary, secondary amines, amides)
and C–H “oop” (aromatics) [43]. The amines and hydroxides func-
tional groups have been shown from previous research to be good
381 corrosion inhibitors [44–46]. The spectra peak after corrosion test
presents the same molecular functional groups at near similar peak
values of 3330.91, 1635.77, 1181.46, 1047.21 and 873.59 cm$^{-1}$.

Comparison of the spectra before and after the corrosion test
382 clearly reveals the decrease in transmittance indicators for the
383 functional groups earlier mentioned, they involved in the electro-
chemical reaction resulting in inhibition of the steel through
384 adsorption. The intensity of the peaks of 1181.46, 1047.21 and
385 873.59 cm$^{-1}$ after the corrosion test significantly decreased due
386 to the strong reaction of the inhibitor molecules at those peaks
387 with the metal through chemical reaction mechanism. The groups
388 instigates the formation of stable chemical precipitates between
389 the substrate metal composition of FSS and MPSB compound. The
390 complexes tend to suppress the corrosion reaction mechanisms
391 inhibiting FSS surface [47].

### Optical microscopy analysis

Optical micrographs of FSS samples before and after the corro-
sion test are shown from Figs. 7a–9c. The micrographs of FSS sam-
392 ples before the test at mag. x4, x40 & x100 are shown in Fig. 7(a)–
393 (c). The micrographs depict the sample surface after undergoing
394 metallographic procedures and clearly reveal the serrated edges
395 after machining. Fig. 8(a) shows the micrograph of the uninhibited
396 FSS after the corrosion test. Morphological deterioration and of
397 the surface topography can be observed due to the redox electro-
398 chemical reactions of corrosive ions present in the acid media. The ions
399 cause the release of valence electrons and diffusion of Fe$^{2+}$ cations
400 into the acid solution. Zooming in on Fig. 8(a), Fig. 8(b) clearly
401

---

**Table 5**

Data for Gibbs free energy, surface coverage and equilibrium constant of adsorption for 0–1.5% MPSB in 2 M H$_2$SO$_4$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>MPSB concentration (%)</th>
<th>Surface coverage (ø)</th>
<th>Equilibrium constant of adsorption (K)</th>
<th>Gibbs free energy, $D^\text{Go}$ (Kjmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>0.25</td>
<td>0.856</td>
<td>854698.9</td>
<td>−43.80</td>
</tr>
<tr>
<td>C</td>
<td>0.5</td>
<td>0.869</td>
<td>473734.9</td>
<td>−42.34</td>
</tr>
<tr>
<td>D</td>
<td>0.75</td>
<td>0.808</td>
<td>200697.9</td>
<td>−40.21</td>
</tr>
<tr>
<td>E</td>
<td>1</td>
<td>0.937</td>
<td>531040.7</td>
<td>−42.62</td>
</tr>
<tr>
<td>F</td>
<td>1.25</td>
<td>0.967</td>
<td>850030.1</td>
<td>−43.79</td>
</tr>
<tr>
<td>G</td>
<td>1.5</td>
<td>0.945</td>
<td>407640.1</td>
<td>−41.96</td>
</tr>
</tbody>
</table>
identifies some specific areas of morphological deterioration especially at the grain boundary. This clearly shows that intergranular corrosion is partly responsible for the corrosion of FSS, micro-pits due to pitting can also be observed though less visible. These observations [Fig. 8(a)–(c)] show that FSS steel cannot be applied in high sulphate containing industrial environments due to rapid deterioration. The micrographs in Fig. 9(a)–(c) contrast the images in Fig. 8(a)–(c); Fig. 9(a)–(d) show the images of FSS samples from the electrolyte with MPSB compound after coupon analysis. The images reveal a slightly worn surface in comparison to the untested specimens in Fig. 7(a)–(c). MPSB compound effectively protected the FSS samples and the images confirms the results obtained from weight loss and potentiodynamic polarization. The combined action of molybdate ions and heteroatoms of the phenolic aldehydes adsorbs onto the steel, reacting with the surface through chemical reaction mechanism.

**Conclusion**

MPSB performed effectively in the acid media inhibiting the corrosion of 3CR12 ferritic stainless steel. The corrosion protection efficiency values of the compound deviated slightly at the concentrations evaluated as a result of the inhibition reaction of the molecular functional groups and heteroatoms of the compounds which influenced the mechanism of the redox electrochemical reactions and protecting the steel from corrosion. The compound was determined to be anodic type inhibitor. Thermodynamic calculations confirm strong chemisorption reaction mechanism and the adsorption aligned with the Langmuir adsorption isotherm. Infrared spectra images confirmed the adsorption of primary and secondary amines and hydroxides onto the steel.

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**References**


