Inhibition effect of rosemary oil on mild steel corrosion in a water-based petrochemical drilling fluid

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Abstract. Corrosion inhibition of carbon steels applied in water-based petrochemical drilling fluid solution (DFS) with non-toxic chemical compounds is an important focus of research. Rosemary oil (ROS) was evaluated for its corrosion inhibition effect on mild steel (MS) in DFS by the potentiodynamic polarization technique and optical microscopy characterization. The corrosion rate data show that ROS effectively inhibited MS corrosion with an average inhibition efficiency above 90%. ROS displayed anodic type inhibition mechanism. The polarization curves displayed the passivation region, which signified the total surface coverage of MS surface. Morphological images of inhibited MS surface significantly differed from the control MS without ROS, whose surface was severely deteriorated by corrosion pits and grooves.

1. Introduction
Corrosion is the major cause factor involved in industrial downtime, fluid leakages, product contamination industrial accidents, costly maintenance, structural weakness and drainage of costly resources emanating from the electrochemical interaction of corrosive anions in industrial solutions on metallic alloy surfaces of machineries, parts and structures. Carbon steel is readily available compared to other steel grades due to its relatively low cost and exhibition of desirable mechanical and physical properties [1, 2]. They have universal application in industries cutting across chemical processing plants, desalination plants, mining and pickling processes, petrochemical, construction, pharmaceutical, energy generating plant, industrial cleaning and oil well acidizing. Application of chemical compounds known as inhibitors significantly reduce the rate of deterioration of metallic alloys, extending their life span during service operations. Most corrosion inhibitors are costly, unsustainable and toxic [3-6]. However, green organic chemical compounds offer effective corrosion inhibition for mild steel. Oil extracts has been studied in the past for its corrosion inhibition effect [7-12]. The major constituents of rosemary oil include bornyl acetate, camphor, borneol, cineole, camphene, alpha-pinene, catechin and excessive amounts quantity of hydrocarbons [13]. This article focuses on study of the inhibition effect of rosemary oil on mild steel corrosion H\textsubscript{2}O based petrochemical drilling fluid.

2. Material and methods
Mild steel (MS) of cylindrical dimension (0.7 cm diameter) was cut into five test specimens. Each specimen was mounted in acrylic, smoothened with emery papers (80, 120, 240, 320, 400, 600, 800 and 1000 grits) and polished with diamond suspension solution to 6um before washing with deionized H\textsubscript{2}O and propanone. Water based drilling fluid solution (DFS) was formulated from the chemical combination of Al\textsubscript{2}H\textsubscript{2}Na\textsubscript{2}O\textsubscript{13}Si\textsubscript{4}, NaOH, Na\textsubscript{2}CO\textsubscript{3} and BaSO\textsubscript{4}. Rosemary oil (ROS) was sourced NOW...
Foods Industry, USA and formulated prepared in volumetric concentrations of 1%, 2%, 3% and 4% per 50 ml of DFS. Potentiodynamic polarization measurement was monitored with Digi-Ivy 2300 potentiostat device at 25°C. Acrylic embedded MS electrodes with visible surface area of 0.38 cm², Pt counter electrode and Ag/AgCl reference electrode were placed in 50 mL of the DFS/ROS solution and linked to the potentiostat-computer interface. Potentiodynamic polarization was done between potentials of -1.5V to 1.5 V and scan rate of 0.0015 V/s. Omax trinocular metallurgical microscope was used to capture, study and compare the images of the inhibited and non-inhibited steel.

3. Theory
The potentiostat device was ascertained for any possible cause of systematic errors. Device calibration and hardware authentication test was done with the results given in Table 1. The results confirm reproducibility of consistent results with expected experimental error from hysteresis to be less than 1%.

| RAM test | Ok |
|---|---|
| Current test results | |
| Sensitivity offset error (0%) | 0% |
| Gain error | 0% |
| Voltage test results | |
| Sensitivity offset error | 0% |
| Gain error | 0% |

Corrosion current density ($J_{cr}$) and corrosion potential ($E_{cr}$) were determined from extrapolation of the Tafel plots (potential versus log current). Corrosion rate ($C_R$) was calculated as shown in equation 1.

$$C_R = \frac{0.00327 \times J_{cr} \times E_a}{D}$$ (1)

where $D$ is the density (g/cm³), $E_a$ represents equivalent weight of MS (g), 0.00327 is the corrosion rate constant, $\eta$ represents the inhibition efficiency (%) calculated from corrosion rate values according the equation below;

$$\eta = 1 - \frac{C_{R1}}{C_{R2}} \times 100$$ (2)

where $C_{R1}$ and $C_{R2}$ are the corrosion rates with and without ROS inhibitor. Polarization resistance, $R_p$ (Ω) was calculated from equation (3) below;

$$R_p = 2.303 \times \frac{B_a B_c}{B_a} + B_c \left[ \frac{1}{I_{cr}} \right]$$ (3)

where $B_a$ is the anodic Tafel slope and $B_c$ is the cathodic Tafel slope (V/dec).

4. Results and discussion

4.1. Potentiodynamic polarization studies

| LCS sample | ROS conc. (%) | LCS $C_R$ (mm/y) (%) | ROS $\xi_F$ (%) | $C_I$ (A) | $C_I$ (A/cm²) | $E_p$ (V) | $R_p$ (Ω) | $B_c$ (V/dec) | $B_a$ (V/dec) |
|---|---|---|---|---|---|---|---|---|---|
| A | 0 | 2.58 | 0 | 2.55E-04 | 2.26E-04 | -0.989 | 100.60 | -7.220 | 0.191 |
| B | 1 | 0.51 | 80.21 | 5.06E-05 | 4.47E-05 | -0.979 | 508.00 | -9.988 | 4.452 |
| C | 2 | 0.12 | 95.34 | 1.19E-05 | 1.05E-05 | -0.900 | 2159.00 | -9.111 | 4.202 |
| D | 3 | 0.13 | 94.90 | 1.30E-05 | 1.15E-05 | -0.926 | 1971.00 | -9.475 | 4.943 |
| E | 4 | 0.16 | 93.63 | 1.63E-05 | 1.44E-05 | -0.950 | 1578.00 | -10.740 | 5.196 |
Table 2 depicts the result from potentiodynamic polarization test of MS in DFS/ROS solution while Figure 1 shows the polarization plot of MS corrosion. Control MS significantly deteriorated with corrosion rate of 2.58 mm/y due to oxidation of MS surface and leading to diffusion of Fe^{2+} into the electrolyte. Addition of ROS to the electrolyte significantly altered the redox electrochemical mechanism resulting in significant decline in corrosion rate of MS to 0.51 mm/y at 1% ROS to 0.16 mm/y at 4% ROS due to the significant inhibition action of ROS. The complex chemical nature of ROS molecules does not allow for allocation of its effective inhibition action to a particular constituent or functional group such as aromatic, oxides, esters, alcohols compounds etc. The presence of heteroatoms within the reactive groups (C=O, C–O, O–H) of the molecules, π-electrons of the aromatic ring and the double bonds (C=C) allows for strong coordination reaction. The molecules of ROS exist as neutral and protonated organic molecules which adsorb onto MS surface. Variation of corrosion potential of the polarization curves between the inhibited and non-inhibited MS samples shows ROS is an anodic type inhibitor whose corrosion inhibition reaction mechanism is by coverage of the entire steel surface. The polarization plots show that ROS inhibiting compound induces passivation on MS signifying film formation which counteracts the action of corrosive anions.

![Figure 1. Potentiodynamic polarization plot of MS corrosion in DFS/ROS (0% - 4% ROS) solution.](image)

4.2. Optical microscopy studies
Figure 2(a) and (b) presents the optical image of MS prior to the corrosion test and immediately after corrosion in the absence of ROS inhibiting compound while Figure 3 depict the morphology of MS after corrosion from DFS/ROS solution. The morphology of MS after corrosion in the absence of the ROS inhibiting compound [Figure 2(b)] shows the presence of grooves, corrosion pits and severe surface degradation as a result of the electrochemical action of O_2 and Cl^- anions in the solution which accelerates the oxidation-reduction reaction mechanism on the steel surface. This mechanism results in selective and general oxidation of the steel surface leading to severely corroded MS steel. ROS inhibited MS surface (figure 3) contrasts the non-inhibited MS surface. There was general surface improvement of MS though the slight contrast between it and that in figure 2(a) is probably due to preadsorption of the corrosive anions before adsorption of protonated ROS molecules leading to complexes which stifled further redox reaction of the steel surface.
Figure 2. Optical microscopy image of (a) MS surface before corrosion test and (b) MS surface after corrosion without ROS.

Figure 3. Optical microscopy image of (a) MS surface after corrosion within the presence of ROS compound.

5. Conclusions
Rosemary oil effectively inhibited the mild steel corrosion in a petrochemical drilling fluid. The inhibition type and properties were observed to be anodic due to surface coverage of the steel. This was quite evident in the passivation region formed on the polarization plot as a result of inhibition the oxidation-reduction reaction mechanism. Optical images obtained confirmed the inhibiting action of rosemary oil with the inhibited surface appearing smooth and well preserved while the non-inhibited surface was severely corroded.

Acknowledgment
The authors appreciate Covenant University, Ogun State, Nigeria for the funding of this research.

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