Effect of Organic Oxygen Scavenger on Performance of Pyrrole as Corrosion Inhibitor

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Abstract. The inhibitory effect of pyrrole in the presence of methyl ethyl ketoxime (MEKO) and erythorbic acid (EA) on the corrosion of carbon steel in static of condition 3.5 wt% NaCl solution were studied using Linear Polarization Resistance (LPR) method. Experimental results found that the inhibition effect of pyrrole increased with the increase of oxygen scavenger concentration. The inhibition efficiency was observed to be about 67% after addition of erythorbic acid (EA) into saline solution containing 100 ppm of pyrrole compared by adding MEKO which recorded about 59%. The addition of oxygen scavenger could reducing the corrosion rate of carbon steel by reacting with dissolved oxygen in the solution and thus further to protect metal surface.

1. Introduction
Corrosion is worth investigating in oilfield application because corrosion problem represent a large portion of the total cost for oil and gas producing companies every year worldwide [1]. Corrosion problem are usually connected with operating problems and equipment maintenance and resulting in severe economic losses [2]. According Garcia et al; the economic costs linked to the corrosion of natural gas sweetening and oil refining plants range between 10 % and 30 % of the maintenance budget [3]. Corrosion inhibitor is a chemical compound which when added to an aqueous system in a small quantity, serves to retard the corrosion rate of a metal exposed to that aqueous media [4]. Compounds containing nitrogen, oxygen, sulphur and phosphorus in system have particularly been reported as efficient corrosion inhibitor [5]. These compounds prevent corrosion by blocking the active corrosion sites either by getting adsorbed, or by forming a protective layer or an insoluble complex on the metal surface [6]. However, in order to improve the inhibitive force and reduce the cost, synergistic effect is an effective method [7]. The previous study had been proven that pyrrole as effective corrosion inhibitors for carbon steel when immersed in saline media [8]. In order to better perform in term of efficiency, the synergistic effect of pyrrole and the addition at various concentrations of methylethyl ketoxime (MEKO) and erythorbic acid (EA) were carried out in the investigative experiment. The objective of research is on the inhibition effect of pyrrole with different addition of concentration of oxygen scavengers into 3.5 wt% NaCl solution at room temperature (25°C) and static condition. This study was conducted using linear polarization resistance (LPR) method.
2. Experimental

2.1 Material and material preparation
The chemical composition of specimen was analyzed using Inductively Coupled Plasma (ICP) and CHNS analyzer. The percentage composition of carbon steel used in this research is as follow: C, 0.06%; Al, 0.092%; Mn, 0.550%; Ni, 0.056%; Cu, 0.350%; Zn, 0.025%; Pb, 0.070%; Cr, 0.064% and iron as remainder. The commercial grade carbon steel was cut into dimension 1 cm x 1 cm x 0.5 cm and the embedded into cold mounting polymer. The nichrome wire was used to solder to the specimen as an electrical connection. The exposed surface of specimen (area 1 cm²) was ground and polished as previous reported. A 3.5 wt% sodium chloride solution was used as the aqueous solution. A 100 ppm pyrrole was used as test corrosion inhibitor and different concentration of MEKO and EA were then added to evaluate the synergistic corrosion inhibition effect on addition to the test inhibitor.

3. Linear polarization resistance (LPR) measurement and surface morphology analysis
In the Linear polarization resistance (LPR) experiment, the working electrode was immersed in beaker containing typically about 900 ml of NaCl solution. All the experiments were performed at room temperature (25 °C) and static condition. The set-up of experiment was equipped with platinum auxiliary electrode (AE) and a reference saturated calomel electrode (SCE) which was connected to working electrode (WE). The LPR measurements were performed by using a VoltaLab, Model PGP 201 and controlled by corrosion analysis software model Voltamaster 4. The working electrode was immersed for 1 hour in experimental solution to obtain stable open circuit potential (OCP). The polarization resistances value, \( R_p \) was determined after 100 ppm pyrrole injected into 3.5 wt% NaCl with an arbitrarily chosen concentration (50 ppm and 200 ppm) of MEKO and EA. The inhibition efficiency was evaluated from the measured value of \( R_p \) according to Equation 1;

\[
IE\% = \left(1 - \frac{R_p}{R_{p0}}\right) \times 100\%
\]

Where \( R_p \) and \( R_{p0} \) are the polarization resistance value with and without addition of MEKO. The surface morphology of carbon steel was examined using Field Emission Scanning Electron Microscope, FESEM (DSM 982 Gemini Supra 40 VP) and Atomic Force Microscope, AFM (XE-100, Park System).

4. Result and Discussion
Comparison of \( R_p \) values with time when immersed in 3.5 wt % NaCl solution containing 100 ppm pyrrole over 1 hour period with selected concentration (50 ppm and 200 ppm) of MEKO and EA is shown in Figure 1. The immersion of 1 hour period indicates that inhibitor can protect the corrosion in short period [9]. It is very clear from the Figure that the value of \( R_p \) was increased in the presence of pyrrole. The value of \( R_p \) is smaller in the uninhibited solution compared to the inhibited, suggested that pyrrole suppressed the dissolution of carbon steel specimen in the aggressive environment [10]. Addition of MEKO to pyrrole is found to increase \( R_p \) by almost twice times that of the pyrrole alone. For instance, the addition of 50 ppm and 200 ppm MEKO to 100 ppm pyrrole increased \( R_p \) from 1.510 kohm.cm² to 3.489 kohm.cm². However, after addition concentration of 200 ppm EA, the \( R_p \) values was increased to 3.489 kohm.cm². The result also shows that combination of pyrrole and MEKO or EA can give the higher corrosion resistance compared to uninhibited solution. It is also reported by I.M Ibrahim et al (2013); that the combination or synergistic effect of fatty amide and hydrazine increased the corrosion resistance and inhibited the corrosion process excellently compared uninhibited solution [11]. In this experiment, Methyl ethyl ketoxime (MEKO) and Erythorbic acid (EA) were selected as an oxygen scavenger which had ability to eliminate the dissolved oxygen molecules in the solution[12]. Oxygen scavenger was added to deplete the maximum possible amount of dissolved oxygen in solution in order to enhance the inhibition efficiency[13]. Methyl ethyl ketoxime (MEKO) is an organic scavenger that reacted to oxygen to produce methyl ethyl ketone (MEK). The reaction with dissolve oxygen is known to occur as shown below.
C₆H₅NOH + ½ O₂                    C₆H₅O + N₂O   + H₂O                                           (2)

Figure 1. Comparison of $R_p$ values with immersion time in pyrrole-inhibited 3.5 wt% NaCl solution between MEKO and EA

The advantages of methyl ethyl ketoxime (MEKO) include a higher thermal stability than other scavengers. MEKO can break down to smaller organic, carbon dioxide and nitrogen compound [14]. Erythorbic acid (EA) is an isomer of vitamin and reported to the react quickly with dissolve oxygen is to form organic acids and water. The reaction with dissolved oxygen as shown below [15].

C₆H₈O₆+ 1/2O₂                             C₆H₆O₆+ H₂O                                                         (3)

By acting as oxygen scavenger, amount of dissolved oxygen molecules available become depleted. With increasing the concentration of MEKO or EA into solution, more oxygen molecules available would react with MEKO or EA thus further protected to the metal surface. Since oxygen molecules that involved in cathodic reaction were decreased, the anodic reaction also will be decreased correspondingly. Table 1 shows the effect of addition oxygen scavengers on the inhibition efficiency that contained 100 ppm of pyrrole. It is observed that after addition of 50 ppm and 200 ppm of MEKO in the inhibited solution, the inhibition efficiency increased. At the higher concentration of 200 ppm EA, the inhibition efficiency reached about 67% compared to addition MEKO into solution which recorded about 59%. It is can be concluded that the addition of MEKO or EA into the inhibited system is intended to enhance their inhibition efficiency due to interaction between pyrrole and both oxygen scavengers [16].

| 100 ppm pyrrole | 100 ppm pyrrole + 50 ppm MEKO | 100 ppm pyrrole + 50 ppm EA | 100 ppm pyrrole + 200 ppm MEKO | 100 ppm pyrrole + 200 ppm EA |
|------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|
| Inhibition efficiency (%) | 30.72                         | 45.26                       | 39.98                         | 59.55                       | 67.21                       |

4.1 FESEM
The FESEM images of carbon steel specimen after 60 minutes immersion in 3.5 wt% of NaCl solution in the absence and presence of oxygen scavengers are shown in Figure 2 at magnification of 500. In Figure 2(a), the sample was immersed in 3.5 wt % NaCl was severely damaged with a lot of surface corroded. Figure 2 (b) shows the sample was containing 100 ppm pyrrole in addition of MEKO. In the presence of MEKO, the surface of steel is less corroded and looks better compared to Figure 2 (a). After the combination of pyrrole with EA, the surface is also looks smoother as shown in Figure 2 (c). It is indicated the pyrrole and both of oxygen scavenger could be work together to cover the metal surface thus giving it a high degree of protection against corrosion.
Figure 2. FESEM images of carbon steel after immersion in (a) 3.5 wt % NaCl (b) 100 ppm pyrrole + 200 ppm MEKO (c) 100 ppm pyrrole + 200 ppm EA

Table 2. EDX analysis on samples.

| Sample                                      | Fe  | O     | Na   | Cl   | C    |
|---------------------------------------------|-----|-------|------|------|------|
| Carbon steel immersed in 3.5 wt% NaCl solution | 79.65 | 17.23 | 1.37 | 0.64 | 1.11 |
| Carbon steel in 100 ppm pyrrole + 200 ppm MEKO | 91.75 | 5.99  | 0.69 | 0.38 | 1.99 |
| Carbon steel in 100 ppm pyrrole + 200 ppm EA | 95.19 | 1.99  | 0.69 | 0.38 | 1.75 |

The EDX analyses are shown in Table 2 show the elemental composition that contained in sample. In Table 2, the data shows the percentages of Fe, O, Na, Cl and C represent the chemical composition on the metal surface. The main points that wanted to highlight here is the percentage of oxygen in sample. The percentage oxygen in sample (b) and (c) are lower compared to (a) was proven that ability of MEKO and EA act as oxygen scavenger to eliminate the dissolved oxygen available in solution thus to reduce corrosion rate.

4.2 AFM
To support the result, the selected of specimen was analyzed by AFM. The three dimensional AFM images of carbon steel specimen after 60 minutes immersion in inhibited solution in the absence and presence of MEKO at static condition and room temperature are as shown in Figure 3.

Figure 3. AFM image of carbon steel after 60 minutes immersion in (a) 3.5 wt% NaCl (b) 100 ppm pyrrole + 200 ppm MEKO (c) 100 ppm pyrrole + 200 ppm EA

Figure 3(a) show surface morphology of the specimen immersed in 3.5 wt% NaCl solution. It shows a lot of corrosion products deposit on metal surface. The average roughness of surface (Ra) was 97 nm. Figure 3(b) is specimen immersed in 100 ppm pyrrole into 3.5 wt % NaCl and give value of Ra is 51 nm. However, after combination of 200 ppm MEKO and EA to the inhibited solution as shown
in Figure 3(b) and 3(c), the surface become smoother compared to previous figure. The Ra value is 26 nm and 12.305 nm respectively.

5. Conclusion
The inhibition efficiency of pyrrole can be further improved by introducing of an oxygen scavenger that is Metylethyl ketoxime (MEKO) and erythorbic acid (EA). By added the different concentrations of oxygen scavenger into the solution, the amount oxygen molecules available in solution become depleted hence can reduce the corrosion rate. The combination of pyrrole with oxygen scavengers has been found to enhance the efficiency of inhibitive effects due to multiple effects of effective corrosion inhibition [17].

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