Keywords: corrosion inhibition; surfactants; vegetable oils; fatty acids; adsorption; mild steel

Corrosion inhibition by surfactant molecules are related to the surfactant’s ability to aggregate at interfaces and in solution. In this article, the adsorption and corrosion inhibition of series of commercial fatty acid surfactants synthesized based on vegetable oils (sunflower, cottonseed, corn and palm oil) onto mild steel is investigated at 50 °C in CO₂-saturated brine. The inhibition efficiencies of the tested compounds showed good inhibition and protection of the carbon steel even at low concentrations. The corrosion inhibition tendency correlated to the chemical structure of the compounds.

Introduction

The study of CO₂ corrosion started a few decades ago and cannot be considered well resolved yet. Carbon steel is widely used as tubing or as pipeline in the oil and gas industry, and is usually eroded heavily, especially when the corrosion electrolyte contains CO₂. In the oil extraction and processing industries, inhibitors have always been considered to be the first line of defense against corrosion. Most of the inhibitors currently used in producing wells are considered to be the first line of defense against corrosion. Organic nitrogenous compounds. Most of the inhibitors currently used in producing wells are considered to be the first line of defense against corrosion. Organic nitrogenous compounds.

In the present work, we have synthesized novel surfactants isolated from vegetable oils (sunflower (A), cottonseed (B), corn (C) and palm (D) oils) and studied their anti-corrosive properties in carbon dioxide environments at 50 °C. The surfactants were prepared in different compositions (Scheme 1) based on vegetable oils and diethanolamine as in Ref. The structures of synthesized surfactants were confirmed by physical-chemical spectroscopic methods.

Scheme 1. Molecular structure of the synthesized anionic surfactants. where M=Na⁺ (Inhibitor I), K⁺ (Inhibitor II), NH₄⁺ (Inhibitor III), -NH-CH₂-CH₂-OH (Inhibitor IV), -N-(CH₂-CH₂-OH)₂ (Inhibitor V).

Experiments

Linear polarization resistance corrosion rate (LPR) (bubble-test method) involves evaluating the corrosion of a given metal in simulated brine saturated with CO₂ at a temperature equivalent to that in the field. During the test, CO₂ gas is sparged continuously into the test solution. The rate of corrosion is determined instantaneously with the LPR technique, in which a small direct-current voltage is applied to a pair of identical electrodes and the resultant current is measured. A limitation of the bubble-test method is that it does not provide information on the effect of shear stress on the performance of a given corrosion inhibitor.

Results and Discussion

Figure 1 shows that, the change in corrosion rate (CR) with time for low carbon steel in 1%NaCl solution saturated with CO₂ containing different concentrations form inhibitor at 50 °C synthesized based on all four oils. The inhibitor was added after 1 hour of exposure because at this time the corrosion potential got stable, allowing the measurement of the corrosion rate (CR) prior the injection of the inhibitor. The initial CR, without inhibitor, was measured to be between 3.45 and 5.03 mm/year. It can be observed from Figure 1 that the CR, in the absence of inhibitor, tends to increase with time. The increase in CR has been attributed to the galvanic effect between the ferrite phase and cementite (Fe₃C) which is a part of the original steel in the non-oxidized state and accumulates on the surface after the preferential dissolution of ferrite (α-Fe) into Fe³⁺ [6]. Fe₃C is known to be less active than the ferrite phase. Therefore, there is a preferential dissolution of ferrite over cementite, working the former as the anode and latter as the cathode, favoring the hydrogen evolved reaction (HER) during the corrosion process.⁶,⁷

Corrosion parameters were calculated on the basis of LPR test. The inhibition efficiency (IE) and degree of surface coverage were calculated according to the following equations:⁵
The results also showed that, the inhibition efficiencies in the case of surfactants obtained on the basis of palm oil are higher compared with those of inhibitors obtained on the basis of cottonseed, corn and sunflower oils at the same conditions. This behavior may be due to the difference in fatty acids compositions of oils. The fatty acid composition of oils from vegetable sources varies depending on plant origin and sort (Table 1).8

\[ IE, \% = 100 \left( \frac{CR_i - CR}{CR_i} \right) \]  
(1)

\[ \theta = 1 - \frac{CR_0}{CR} \]  
(2)

where

- \( \theta \) = Surface coverage,
- \( CR_0 \) is the corrosion rate without inhibitor and
- \( CR \) the corrosion rate when inhibitor is present.

It can be seen that the presence of inhibitors results a high decrease in the rate of corrosion. In the case of these surfactants, the corrosion rate decreases as the inhibitor concentration increases, getting maximum inhibition efficiency ranged between 91.9 and 99.90 % at 100 ppm after 20 hour of exposure.

The results showed that all synthesized inhibitors were good inhibitors and their inhibition efficiencies were significantly increased with increasing the concentration of surfactant. The increase of inhibitor efficiency with increasing the concentration can be interpreted on the basis of adsorption amount of surfactants on carbon steel increase concentration. This indicates that the inhibitory action of the investigated inhibitors against carbon steel corrosion can be attributed to the adsorption of these molecules on the metal surface, limits the dissolution of carbon steel, and the adsorption amounts of surfactants on carbon steel increase with concentrations in the corrosive solutions.

\[ \frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}} \]  
(3)

Where

- \( K_{ads} \) is the equilibrium constant of the inhibitor adsorption process and
- \( C_{inh} \) is the inhibitor concentration.

Plots of \( C_{inh}/\theta \) versus \( C_{inh} \) yielded a straight line as shown in Fig. 2, which suggested that the adsorption of inhibitors on metal surface obeyed Langmuir adsorption isotherm model. This isotherm assumed that the adsorbed molecules occupied only one site and there was no interaction with other molecules adsorbed. The linear regression coefficients \( (R^2) \) and the slopes parameter variations were calculated. All correlation coefficient \( (R^2>0.9597) \) indicated that the inhibition of carbon steel by these inhibitors was attributed to the adsorption of surfactant molecule on the metal surface. However, the slopes of the \( C_{inh}/\theta \) versus \( C_{inh} \) plots were close to 1 and showed a little deviation from unity which meant non-ideal simulating12 and unexpected from Langmuir adsorption isotherm. They might be the results of the interactions between the adsorbed species on the metal surface.13, 14
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Table 1. Fatty acid composition of the oils (percent by weight of total fatty acids).

<table>
<thead>
<tr>
<th>Oil</th>
<th>Unsatd/Satd. ratio</th>
<th>Saturated acids</th>
<th>Unsaturated acids</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Capric C10:0</td>
<td>Laurie C12:0</td>
</tr>
<tr>
<td>Sunflower (A)</td>
<td>7.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cottonseed (B)</td>
<td>2.8</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Corn (C)</td>
<td>6.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Palm (D)</td>
<td>1.0</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>

The values of $K$ obtained from the Langmuir adsorption isotherm are calculated, together with the values of the Gibbs free energy of adsorption ($\Delta G^0_{ads}$) calculated from

$$K_{ads} = \frac{1}{55.5} \exp \left( - \frac{\Delta G^0_{ads}}{RT} \right)$$  (4)

where

- $R$ is the universal gas constant,
- $T$ the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution.

The high values of $K_{ads}$ for the studied surfactants indicate stronger adsorption on the metal surface in CO$_2$-saturated brine. Large values of $K_{ads}$ imply more efficient adsorption and hence better inhibition efficiency.\(^4\) The large value of $K_{ads}$ obtained for the studied surfactants agree with the high inhibition efficiency obtained.

The negative $\Delta G^0_{ads}$ values are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the carbon steel surface. Generally, values of $\Delta G^0_{ads}$ up to -20 kJ mol$^{-1}$, the types of adsorption was regarded as physisorption, the inhibition acted due to the electrostatic interactions between the charged molecules and the charged metal, while the values around -40 kJ mol$^{-1}$ or smaller were associated with chemisorption as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of bond (chemisorption).\(^5\) The values of $\Delta G^0_{ads}$ in our measurements for all inhibitors synthesized based on all oils were found around -40 kJ mol$^{-1}$, thus the adsorption mechanism of the surfactants on carbon steel in 1% NaCl solution saturated with CO$_2$ was typical chemisorption.

Conclusions

Linear polarization corrosion rate was employed to study the corrosion inhibition of carbon steel in CO$_2$-saturated solutions using some novel surfactants as corrosion inhibitors synthesized based on vegetable oils.

All inhibitors were found to be effective inhibitors for carbon steel corrosion in CO$_2$-saturated solutions.

References

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