SYNTHESIS OF OXYGENATED ETHYL ESTERS OF TALL OIL FATTY ESTERS
AND CharacterIZATION OF THEIR PROPERTIES
AS CORROSION INHIBITOR TO MILD STEEL

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ABSTRACT

A fractional factorial experimental design was used to determine the optimum values of temperature, content of the catalyst, content of ethanol, and time of the reaction for the synthesis the oxygenated ethyl esters of tall oil fatty acids. The inhibition effect of the oxygenated ethyl esters of tall oil fatty acids on the corrosion of mild steel in 1.0 M HCl water solutions was investigated by mass loss and electrochemical measurements. The effect of temperature on the corrosion behaviour of mild steel in the presence of 0.5 g l^-1 of the oxygenated ethyl esters was studied in the temperature range from 25 to 75 °C. Results obtained revealed that the oxygenated ethyl esters performed excellently as a corrosion inhibitor for mild steel in HCl solution.

Keywords: Corrosion inhibitor; hydrochloric acid; mild steel; oxygenated ester; tall oil fatty acids.

INTRODUCTION

Acid solutions are widely used for industrial cleaning, oil well acidification and pickling. The corrosion of steel in such applications and its inhibition constitute a complex problem. Generally, using organic inhibitors to mitigate corrosion of mild steel in acidic media is highly cost-effective [1]. During the past 15 years, the inhibition of steel by different types of organic inhibitors has been extensively studied [2-6]. A perusal of the literature on acid corrosion inhibitors reveals that most organic substances employed can adsorb on the metal surface through nitrogen, oxygen, sulphur and phosphorus, multiple bonds or arene rings, block the active sites and decrease the corrosion rate [7-14]. In view of the excellent performance of the esters of tall oil fatty acids [15-16], the present authors have synthesized oxygenated ethyl esters of these acids, with the objective to evaluate their corrosion inhibition properties on mild steel in 1.0 M HCl solution.

EXPERIMENTAL

Hydrochloric acid and doubly distilled water were used for preparing the aggressive solutions (1.0 M HCl) for all experiments. The composition of tall oil fatty acids is: stearic acid – 18.0 %; palmitic acid -24.0 %; oleic acid - 38.0 % and linoleic acid - 20.0 %.

An experimental design was used to determine the optimum values of temperature, content of the catalyst, content of ethanol, and time of the reaction. A 2^1 fractional factorial design with the four variables studied at two levels by performing eight experiments was chosen. The response was the degree of conversion of tall oil fatty acids to ethyl esters. The design matrix (Table 1) shows the coded values for the two levels of the variables and the response values. The catalyst chosen for the experiments was sodium ethoxide.

The experiments were performed in conical flasks using 150 milliliters of tall oil fatty acids. The catalyst (0.5 or 1% mass of the amount of the acids of sodium
ethoxide) was first dissolved in 72 ml of ethanol, which represented a 100 % excess of the stoichiometric amount required for the experiment. It was necessary to heat the ethanol slightly with stirring to completely dissolve the catalyst. The required amounts of ethanol and dissolved catalyst were then added to the oil and stirring was initiated. Samples of approximately 3 - 4 ml of the reaction mixture were pipetted out at 60 and 120 minutes respectively. The reaction in the samples was arrested by adding one or two drops of water and they were analyzed to determine the degree of completion of the reaction.

After the end of reaction time the reaction was stopped and the reaction mixture was allowed to stand overnight while phase separation occurred. The ester phase was then decanted from the equilibrium mixture.

The excess alcohol and residual catalyst were washed from the ester with water in a glass column (1.26 cm in diameter and 100 cm in length). Water was sprayed at the top of the column at a low velocity to remove the excess of alcohol and catalyst as it percolated through the column. During the washing, some of the ester formed an emulsion with the water; a time of 24-48 hours was required for the water phase (containing alcohol, catalyst and emulsified ester) to settle and the ester phase to become clear. In the end of the process water was removed by vacuum distillation.

High Performance Liquid Chromatography (HPLC) was used to determine the composition of the reaction mixture and the degree of conversion. The composition of the ester mixture was determined by Gas Chromatography (GC).

The ethyl esters of the tall oil fatty acids were further subjected to oxidation to introduce functional OH-groups by the following method: 1.0 cm$^3$ 0.5 % solution of KMnO$_4$ and 1 cm$^3$ of the ethyl ester were mixed in a test tube, and stirred manually. After some time, the pink color of KMnO$_4$ disappeared and a brown precipitate of manganese dioxide was formed. The reaction is shown as:

\[
\begin{align*}
R-\text{CH} & \equiv \text{CH}-(\text{CH}_2)_n-\text{COOC}_2\text{H}_5 \\
\text{KMnO}_4 & \rightarrow R-\text{CH} \equiv \text{CH}-(\text{CH}_2)_n-\text{COOC}_2\text{H}_5
\end{align*}
\]

Mild steel coupons of size 4.0 x 2.0 x 0.3 cm having composition (% _\text{max}_) 0.16 % C, 0.10 % Si, 0.40 % Mn, 0.02 % S, 0.013 % P, and the remainder Fe were used for the corrosion studies. Before each corrosion experiment, the coupons were mechanically polished with silicon carbide abrasive paper, washed with deionized water, degreased with acetone, dried at room temperature. Then they were placed in the test solution. After 4 hours of immersion, the coupons were withdrawn, washed, dried and reweighed. The mass loss of the mild steel coupons in 1.0 M HCl with and without the addition of different concentrations of oxygenated ethyl ester of tall oil fatty acids was used to calculate the corrosion rate in g m$^{-2}$h$^{-1}$.

**RESULTS AND DISCUSSION**

The results obtained from the eight experiments performed according to the fractional factorial design (Table 1) were analyzed using the Statistical Analysis System (SAS) software version 9.1.3 to develop the following equation, which shows the dependence of the degree of conversion, reaction time, temperature, content of ethanol and content of catalyst:

\[
\text{CONV} = 59.51 - 1.28t + 20.6T + 5.01A + 6.91tT + 5.31tC + 2.96tA
\]

where: $t =$ reaction time, minutes; $T = $ temperature, Celsius; $A = $ content of catalyst, % by the mass of the acids; $A =$ content of alcohol, ml, and CONV = percentage conversion of tall oil fatty acids to ester.

Table 1 shows the experimental data and data, calculated from the model (1). First, we calculated the dispersion by:

\[
S_u^2 = \frac{1}{n-1} \sum_{i=1}^{n} (y_{uk} - y_u)^2 \quad (2)
\]

Then we calculated the test of Cohen ($G$) by:

\[
G = \frac{\max S_u^2}{\sum_{u=1}^{N} S_u^2} = 0.19 \quad (3)
\]

From the table data [17] we got the critical value for the $G -$ test (0.5157). Because of the $G < G_c$, we calculated the dispersion of the experimental data by:

\[
S_e^2 = \frac{1}{N} \sum_{u=1}^{N} S_u^2 = 0.16 \quad (4)
\]
Table 1. Matrix for the experimental design.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Levels</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low (-1)</td>
<td>High (+1)</td>
<td></td>
</tr>
<tr>
<td>1 Reaction time (x₁), minutes</td>
<td>60</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>2 Temperature (x₂), °C</td>
<td>25</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>3 Content of the catalyst (x₃), %</td>
<td>0.5</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>4 Content of the alcohol (x₄), cm³</td>
<td>36</td>
<td>72</td>
<td></td>
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</table>

Experimental design  Conversions  Dispersion,

<table>
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<tr>
<th>No</th>
<th>x₁</th>
<th>x₂</th>
<th>x₃</th>
<th>x₄</th>
<th>y₁</th>
<th>y₂</th>
<th>y₃</th>
<th>ȳ</th>
<th>ŷᵣ</th>
<th>ŷᵤ</th>
<th>sᵤ²</th>
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<tbody>
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<td>1</td>
<td>1</td>
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<td>-1</td>
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<td>28.0</td>
<td>29.0</td>
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<td>28.58</td>
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<td>1</td>
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<td>51.00</td>
<td>50.91</td>
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<td>1</td>
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<td>81.5</td>
<td>81.5</td>
<td>81.40</td>
<td>81.31</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>98.1</td>
<td>98.6</td>
<td>98.5</td>
<td>98.40</td>
<td>98.48</td>
<td>0.07</td>
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\( \bar{y} \) - Average value for the conversion, %;  \( \hat{y}_u \) - Value calculated by the model, %.

The significance of the coefficients in the eq. 1 was determined by t-test. From the table data [17] we got the critical value for the t - test (2.306). Then we calculated the \( t_{cr}S_b \) by:

\[
t_{cr}S_b = 2.306 \sqrt{\frac{S^2_L}{nN}} = 0.19
\]

Because of fact that all coefficients in eq. 1 have value more than 0.19 they are significant. After that we calculated the sum of squares of insufficiency \( Q_L \) by:

\[
Q_L = n \sum_{i=1}^{N} (y^2 - y)^2
\]

From the table data [17] we calculated the dispersion of insufficiency \( S_L^2 \) by:

\[
S_L^2 = \frac{Q_L}{v_L}
\]

The calculated F-test from our data is:

\[
F = \frac{S_L^2}{S_e^2} = 1.17
\]

The critical value for the F-test was 4.12 [17]. Because of fact that the calculated value of F-test is less than the critical value of F-test from [17] our model (1) is adequate of the experimental data.

The inspection of eq. 1 shows that the temperature is the most important independent factor affecting the degree of conversion. The combined influences of temperature and time of reaction, and the content of the catalyst and the content of the alcohol are also significant.
Table 2. Electrochemical parameters and protection efficiency for mild steel in 1.0 M HCl containing different concentrations of oxygenated ethyl ester of tall oil fatty acids at 25°C.

<table>
<thead>
<tr>
<th>Concentration, ( g \text{l}^{-1} )</th>
<th>Corrosion potential, ( E_{\text{corr}} ), mV</th>
<th>Corrosion current density, ( i_{\text{corr}} ), mA cm(^{-2} )</th>
<th>Anodic tafel slope, ( b_a ), mV dec(^{-1} )</th>
<th>Cathodic tafel slope, ( b_c ), mV dec(^{-1} )</th>
<th>Protection efficiency, ( P ), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>- 505</td>
<td>0.271</td>
<td>47</td>
<td>78</td>
<td>—</td>
</tr>
<tr>
<td>0.05</td>
<td>- 515</td>
<td>0.051</td>
<td>52</td>
<td>62</td>
<td>84.23</td>
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<tr>
<td>0.10</td>
<td>- 523</td>
<td>0.034</td>
<td>53</td>
<td>63</td>
<td>88.86</td>
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<tr>
<td>0.20</td>
<td>- 525</td>
<td>0.025</td>
<td>51</td>
<td>71</td>
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<tr>
<td>0.30</td>
<td>- 531</td>
<td>0.022</td>
<td>52</td>
<td>64</td>
<td>92.11</td>
</tr>
<tr>
<td>0.40</td>
<td>- 533</td>
<td>0.021</td>
<td>53</td>
<td>63</td>
<td>92.65</td>
</tr>
<tr>
<td>0.50</td>
<td>- 537</td>
<td>0.020</td>
<td>52</td>
<td>69</td>
<td>93.01</td>
</tr>
</tbody>
</table>

Using the method of Box-Wilson we optimized the conversion of ethyl ester, and obtained the optimal parameters for highest conversion: 89 minutes, 75 Celsius, 0.75 % of the catalyst used, and 58.4 milliliters of the alcohol used. Then the conversion is 99.1 %.

The protection efficiency (\( P \)) was determined by using the following equation:

\[
P\% = 100 \times \left( W - W_{\text{corr}} \right)/W,
\]

where: \( W \) and \( W_{\text{corr}} \) stand for the mass loss of the mild steel coupons in an uninhibited and an inhibited solution, respectively.

The protection efficiency as a function of the concentration of oxygenized ethyl ester of tall oil fatty acids at room temperature (25°C) is plotted in Figure 1. It can be observed from Fig. 1 that the protection efficiency increases with the increase of the concentration of the inhibitor studied from 0.05 to 0.5 g l\(^{-1} \). A visual examination was carried out after the mass loss measurements. While in the absence of inhibitor, a uniform corrosion attack was observed, in the presence of the inhibitor, there was no generalized attack, the surface was bright and did not present any corrosion form.

Electrochemical corrosion parameters such as the corrosion potential (\( E_{\text{corr}} \)), the anodic and cathodic Tafel slopes (\( b_a, b_c \)), the corrosion current density (\( i_{\text{corr}} \)) and the protection efficiency (\( P \% \)) for acid solutions with increasing concentrations of the inhibitor were determined as described in [18-20]. The obtained results are presented in Table 2. It can be seen from the experimental results that oxygenated ethyl ester of tall oil fatty acids decreased the corrosion current density significantly at all the studied concentrations. The presence of oxidized ethyl ester of tall oil fatty acids resulted in a slight shift of the corrosion potential towards the active direction in comparison to the result obtained in the absence of the inhibitor. Both the anodic and cathodic current densities were decreased indicating that oxygenated ethyl ester of tall oil fatty acids suppressed both the anodic and cathodic reactions.

The surface coverage \( h \) was calculated from the following equation:

\[
\eta = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0},
\]

where \( i_{\text{corr}}^0 \) and \( i_{\text{corr}} \) are the uninhibited and inhibited corrosion current densities, respectively.

The protection efficiency (\( P \% \)) of the oxygenated ethyl ester of tallic acids was obtained from the following equation:

\[
P\% = \eta \times 100
\]

The almost unchanged Tafel slopes \( b_a \) and \( b_c \) in the presence of oxygenated ethyl esters of tall oil fatty acids indicate that the inhibitor acted by merely blocking the reaction cites of the metal surface without changing the anodic and cathodic reaction mechanisms.

The corrosion reaction can be regarded as an Arrhenius-type process, the rate of which is given by:

\[
i_{\text{corr}} = A \exp(-E_A/RT)
\]

where \( i_{\text{corr}} \) is the corrosion current density, \( A \) the Arrhenius pre-exponential constant and \( E_A \) the activation energy for the corrosion process. Arrhenius plots
for the corrosion current density of mild steel are given in Fig. 2. It can be seen that the corrosion current density for mild steel increases more rapidly with temperature in the uninhibited solution than in the inhibited solution. This result confirms that the oxigenated ethyl esters of tall oil fatty acids act as an efficient corrosion inhibitor in the range of temperature studied. The calculated values of the apparent activation corrosion energies in the absence and presence of the inhibitor are 46 and 62 KJ mol$^{-1}$, respectively. The high activation energy value in the presence of oxigenated ethyl esters of tall oil fatty acids supports the results obtained from the mass loss measurements and indicates high protection efficiency of the inhibitor.

In order to investigate the retention of the protection provided by the oxigenated ethyl ester of tall oil fatty acids, the mild steel samples taken out of the acid solutions containing 0.5 gl$^{-1}$ oxigenated ethyl esters of tall oil fatty acids after mass loss measurements were dried in a desiccator for different times, then transferred into fresh 1.0 M HCl solutions without inhibitor for 2 hours of immersion time. Figure 3 shows the variation of protection efficiency with the drying time. It can be seen that the protection provided by the oxigenated ethyl esters of tall oil fatty acids was retained and the degree of protection decreased with increasing the drying time.

**CONCLUSIONS**

- The oxigenated ethyl esters of tall oil fatty acids inhibit the corrosion of mild steel in 1.0 M HCl medium.
- The oxigenated ethyl esters of tall oil fatty acids were found to affect the anodic and cathodic pro-

\[ (1/T) \times 10^3 (K^{-1}) \]

\[ \text{Protection efficiency, } \% \]

\[ \text{Time, hour} \]

\[ \text{Protection efficiency, } \% \]

\[ \text{Concentration, gl}^{-1} \]

\[ 80 \]

\[ 90 \]

\[ 92 \]

\[ 94 \]

\[ 0 \]

\[ 0.1 \]

\[ 0.2 \]

\[ 0.3 \]

\[ 0.4 \]

\[ 0.5 \]

\[ 0.6 \]

\[ 80 \]

\[ 82 \]

\[ 84 \]

\[ 86 \]

\[ 88 \]

\[ 90 \]

\[ 92 \]

\[ 94 \]

\[ 0 \]

\[ 1 \]

\[ 2 \]

\[ 3 \]

\[ 4 \]

\[ 5 \]

\[ 6 \]

\[ 7 \]

\[ 50 \]

\[ 60 \]

\[ 70 \]

\[ 80 \]

\[ 90 \]

\[ 100 \]

\[ 2.8 \]

\[ 2.9 \]

\[ 3.0 \]

\[ 3.1 \]

\[ 3.2 \]

\[ 3.3 \]

\[ 3.4 \]

\[ -1 \]

\[ -2 \]

\[ -3 \]

\[ -4 \]

\[ -5 \]

**REFERENCES**


Fig. 1. Variation of the protection efficiency with inhibitor concentration for mild steel in 1.0 M HCl.

Fig. 2. Arrhenius slopes calculated from the corrosion current density for mild steel in: (a) 1.0 M HCl and (b) 1.0 M HCl + 0.5 g l$^{-1}$ oxigenated ethyl esters of tall oil fatty acids.

Fig. 3. Variation of the protection efficiency with drying time for mild steel samples after the mass loss measurements in the presence of oxigenated ethyl esters of tall oil fatty acids at 25°C.

cesses and their inhibition efficiency increased with the increase of the inhibitor concentration.
- The addition of oxigenated ethyl esters of tall oil fatty acids to 1.0 M HCl leads to an increase of the apparent activation corrosion energy value determined from the temperature dependence of the corrosion current density.
- The inhibition of corrosion by the oxigenated ethyl esters of tall oil fatty acids is due to the formation of chemisorbed films on the metal surface.
17. D. Kamenski, V. Kornjushko, Mathematical modeling and optimization of chemical processes, University “Prof. Dr. Assen Zlatarov”, Bourgas, 1982, (in Bulgarian).