In this paper, we compared the corrosion inhibiting effect of two essential oils on mild steel in 1 M HCl. The essential oils are extracted from natural plants harvested in Morocco and prepared through distillation. To carry out this work, we used gravimetric and electrochemical methods, including current-potential plots and impedance spectroscopy. The results obtained show that both essential oils are a good corrosion inhibitor and that the inhibition efficiency of wormwood essential oil reaches a value of more than 80% at 298 K. To learn the fundamentals of how inhibitors interact with metal surfaces, wormwood essential oil adsorption on a mild steel surface was also investigated. The Langmuir isotherm model is revealed to be how the essential oils adsorb on the metal surface. The effect of temperature on the performance of mild steel in 1 M HCl with wormwood essential oil was examined in the temperature range of 313 to 353 K. Additionally, calculations and discussions are made to provide some thermodynamic data for the adsorption processes. This work enters the framework for the use of non-toxic products in green chemistry.

Keywords: mild steel, acid corrosion, gravimetric study, electrochemical study, tafel plots.

INTRODUCTION

Green technologies are regarded as being ecologically beneficial when it comes to their supply chain or production process. It is a method of producing energy that is less damaging to the environment than traditional techniques. Acidic solutions are widely used in industry, in various fields such as acid brining, industrial cleaning, acid scaling and in petrochemical industries [1 - 8]. However, these solutions are very corrosive. Because of the general aggressiveness of the acidic solution, it is generally recommended to use an inhibitor to reduce the corrosive attack of media on metallic materials. Indeed, several types of organic compounds, mainly containing electronegative functional groups and π electrons, of a conjugated double or triple bond, exhibit an inhibitory effect on the corrosion of iron. Recent literature is brimming with studies investigating various plant extracts for uses like corrosion inhibition [9 - 18].

Numerous essential oils (EOs) are abundant in aromatic components and are derived from various plant sections [19 - 21]. A range of these EOs have proven their
ability to act as inhibitors of corrosion for various alloys and metals in various corrosive environments [22 - 27]. In this frame we are interested to study the inhibition of corrosion of mild steel in 1M HCl medium by two EOs, the first is wormwood EO, (Anethum graveolens) and the second dill EO (Artemisia absinthium) by coupling gravimetric and electrochemical measurements.

EXPERIMENTAL

By diluting the concentrated acid, d = 1.19 and 37 wt. % of Riedel Haen brand with distilled water, the concentration of hydrochloric acid is kept at 1 mol L\(^{-1}\). EOs are added at a concentration of between 0.5 and 2.5 g L\(^{-1}\).

Pre-treatment of the samples

Table 1 lists the various elements that are present in mild steel samples.

For the electrochemical studies, we employed a surface of 1 cm\(^2\), whereas the mild steel samples were mechanically cut into dimensions of 1 cm \(\times\) 5 cm \(\times\) 0.06 cm for the gravimetric measurement. The samples were manually polished (grades 400, 800 and 1200) on wet SiC paper before each measurement, rinsed with double distilled water, ultrasonically cleaned in alcohol for 5 min. The samples were then left to air dry.

Preparation of plant extracts

The wormwood and dill EOs, endemic or native to Morocco (An endemic species is a species whose natural range without human intervention is a limited geographical region), were prepared through distillation and identified using gas chromatography-mass spectrometry (GC-MS).

Evaluation methods

Gravimetric measurement

After being submerged in acid for 6 hours at 298 K, the weight loss of steel with and without the addition of various EOs concentrations was calculated.

The relationship (1) is used to calculate the steel’s corrosion rate \(V\):

\[
V_{\text{corr}} = \frac{\Delta m}{S \cdot t} \quad \text{(mg.cm}^{-2} \cdot \text{h}^{-1})
\]  

(1)

where: \(S\) - the sample’s surface area in cm\(^2\), \(m\) - the mass loss given in mg, and \(t\) - the immersion period in hours.

Eq. (2) was used to calculate the inhibitory efficiency as a percentage (E %):

\[
E\% = \frac{V_{\text{corr}} - V_{\text{inh}}}{V_{\text{corr}}} \times 100
\]

(2)

where \(V_{\text{corr}}\) and \(V_{\text{inh}}\) represent the weight losses due to steel corrosion following immersion in inhibitor-containing and inhibitor-free solutions.

Electrochemical measurement

Voltamaster 4 software was used to control a potentiostat (PGZ 100) used to monitor electrochemical experiments. Three-electrode Pyrex glass cells with thermostatic jackets were used for the electrochemical measurements. The working electrode was a mild steel rod with a surface area of 1 cm\(^2\). The reference electrode was a saturated calomel electrode Hg/Hg\(_2\)Cl\(_2\)/KCl (SCE), and the counter electrode was a platinum foil with a surface area of 3 cm \(\times\) 3 cm. After 30 minutes of immersion, impedance measurements were made at corrosion potential, the sinusoidal voltage’s amplitude is 10 mV peak to peak at frequencies between 100 kHz and 10 mHz. Potentiodynamic polarisation experiments were carried out in the potential range of -750 mV to -100 mV/SCE at a scanning rate of 1 mV.s\(^{-1}\).

RESULTS AND DISCUSSION

Weight loss measurements

Table 2 presents an overview of the study’s findings. According to a review of Table 2, the corrosion rate for both inhibitors decreases as the inhibitor concentration rises. For wormwood EO, the maximal inhibitory efficiency is 88 % at 2 g.L\(^{-1}\), and for dill EO, it is 86 % at 2.5 g.L\(^{-1}\).
The evaluation of corrosion inhibition by gravimetric measurements show that the two oils are good inhibitors of steel in acid environment and its effectiveness exceeds 80%.

**Polarization measurements**

The cathodic and anodic polarisation plots of the steel in a 1 M HCl solution, devoid and containing the tested EOs at varied concentrations, are shown in Fig. 1.

The examination of Fig.1(a) demonstrates that the addition of wormwood EO diverts the polarization potentials towards the negative values, this remark is a proof that does not protect the entire mild steel surface, on the other side Fig.2(b) shows that the addition of dill EO does not change the potential.

It is clear from the different polarization curves that the corrosion current is remarkably affected in the cathodic branches. The addition of inhibitors results in a decrease in both cathodic and corrosion current densities. This decrease is even more marked than the concentration of compound added to the 1M HCl solution. The Tafel law is clearly validated by the large linearity range displayed by the cathodic curves. The proton discharge is then done according to pure activation kinetics. In the anode domain, it is noted that the inhibitory effect for the two EOs tested is noticeable in the vicinity of $E_{\text{corr}}$. Beyond any inhibitory effect is felt, the curves in the absence and in the presence of inhibitors are virtually confused. The two EOs are mixed inhibitors but predominantly cathodic.

The electrochemical parameters, including the corrosion current density ($i_{\text{corr}}$), corrosion potential ($E_{\text{corr}}$), and Tafel cathodic slope ($\beta_c$), are reported in Table 3 and were obtained by polarisation experiments at various concentrations of the EOs under examination. The corrosion efficiency of the inhibitors is calculated from relationship (3).

$$\text{E\%} = \frac{i_{\text{corr}} - i_{\text{inh}}}{i_{\text{corr}}} \times 100 \quad (3)$$

where $i_{\text{corr}}$ and $i_{\text{inh}}$ stand for the corrosion current densities obtained by extrapolating Tafel straight lines in a media containing 1 M HCl, without and with EOs, respectively.

The following observations can be made based on the examination of Table 3:

- The corrosion current density decreases as the concentration increases.
- Overall, both EOs shift the corrosion potential towards more negative values as their concentration increases.
- The two EOs are cathodic-dominant mixed inhibitors.
- As evidenced by the little variations in (c) values, the inhibitor additions have no effect on the cathodic hydrogen evolution reaction mechanism. This suggests activation-controlled hydrogen evolution [28 - 29].
- The corrosion efficiency of two essential oils increases with increasing concentration.

### Table 2. Corrosion rate of steel in 1M HCl medium, in the presence and absence of inhibitors, and corresponding inhibition efficiencies (by weight loss measurements).

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>C (g.L$^{-1}$)</th>
<th>$V_{\text{corr}}$ (mg.cm$^{-2}$.h$^{-1}$)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>0.747</td>
<td>----</td>
</tr>
<tr>
<td>Wormwood EO</td>
<td>0.5</td>
<td>0.236</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.141</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>0.119</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.086</td>
<td>88</td>
</tr>
<tr>
<td>Dill EO</td>
<td>0.5</td>
<td>1.492</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.248</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>0.156</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.118</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>0.101</td>
<td>86</td>
</tr>
</tbody>
</table>
Electrochemical impedance spectroscopy (EIS)

EIS was used to assess the corrosion of mild steel in a 1 M HCl solution after the addition of the inhibitor under investigation. Fig. 2 shows the Nyquist plots of mild steel in 1 M HCl solutions with different concentrations of essential oil. The frequency dispersion is the reason for the discrepancy between the impedance spectra produced and the perfect semicircles [30 - 32].

The shape of these diagrams is the same for the different concentrations in wormwood essential oil
Yassine Elkhotfi, Jallal Zoubir, Issam Forsal, Abdessamad Tounsi

The plots are characterized by a single capacitive loop, corresponding to a charge transfer process. The size of the loop is enhanced by the concentration of the inhibitor. The difference in impedance between lower and higher frequencies is used to compute the transfer resistance values ($R_t$) [33]. The frequency (-$Z''_{\text{max}}$) at which the imaginary component of the impedance is maximal is given by Eq. (4) as well as the double layer capacitance ($C_{dl}$).

$$f(-Z''_{\text{max}}) = \frac{1}{2\pi C_{dl} R_t}$$  \hspace{1cm} (4)

E % is calculated from $R_t$ according to the formula (5).

$$E\% = \left( \frac{R_{t'} - R_t}{R_t} \right) \times 100$$  \hspace{1cm} (5)

where $R_t$ and $R_{t'}$ are the transfer resistances for mild steel in 1 M HCl, respectively, with and without inhibitor.

Table 4 shows that while $C_{dl}$ reduces as the amount of EO increases, $R_t$ tends to increase with the concentration of the inhibitor. The reduction in active surface brought on by the inhibitor’s adsorption at the steel surface can be used to explain the decrease in $C_{dl}$ [34].

The findings of the electrochemical investigation support those of the weight loss measurements. Dill EO has an efficacy of 86 % and wormwood EO has a maximum efficiency of 79 % when used as an inhibitor in 1 M HCl.

**Effect of temperature**

In this section, we investigated the effect of temperature on the rate of steel corrosion inhibition by wormwood and dill EOs using mass loss measurements to determine activation energies. Using mass loss measurements at various temperatures between 313 and 343 K, the influence of temperature on the rate of steel corrosion inhibition was investigated in order to identify activation energies and understand the mechanism of inhibition. Dill EO and wormwood EO were examined at concentrations of 2.5 g L$^{-1}$ and 2 g L$^{-1}$, respectively. Table 5 reports the corrosion rate and inhibition efficiency. The results in Table 5 show that:

- In both the absence and presence of inhibitors, the corrosion rate increases as a function of temperature.
- In the white medium, this increase happens quite quickly.

<table>
<thead>
<tr>
<th>Concentration (g.L$^{-1}$)</th>
<th>$R_t$ (Ô.cm²)</th>
<th>$f_{\text{max}}$ (Hz)</th>
<th>$C_{dl}$ (F.cm$^{-2}$)</th>
<th>E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>60</td>
<td>32</td>
<td>77</td>
</tr>
<tr>
<td>Wormwood EO</td>
<td>0.5</td>
<td>196</td>
<td>40</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>201</td>
<td>25</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>278</td>
<td>13</td>
<td>29</td>
</tr>
<tr>
<td>Dill EO</td>
<td>0.5</td>
<td>262</td>
<td>12</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>318</td>
<td>13</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>418</td>
<td>10</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 4. Characteristic parameters evaluated from the impedance specta for steel in 1M HCl, at various oil concentrations and calculated values of E (%) by EIS method.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>HCl</th>
<th>Wormwood EO</th>
<th>Dill EO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_o$ (mg cm$^{-2}$.h$^{-1}$)</td>
<td>$V$ (mg cm$^{-2}$.h$^{-1}$)</td>
<td>E (%)</td>
</tr>
<tr>
<td>313</td>
<td>1.42</td>
<td>0.23</td>
<td>84</td>
</tr>
<tr>
<td>323</td>
<td>2.64</td>
<td>0.42</td>
<td>84</td>
</tr>
<tr>
<td>333</td>
<td>5.43</td>
<td>0.88</td>
<td>83</td>
</tr>
<tr>
<td>343</td>
<td>10.92</td>
<td>2.1</td>
<td>81</td>
</tr>
<tr>
<td>353</td>
<td>21.98</td>
<td>5.5</td>
<td>75</td>
</tr>
</tbody>
</table>

Table 5. Influence of temperature on corrosion of steel in HCl without and with addition of 2 g.L$^{-1}$ for wormwood EO and 2.5 g.L$^{-1}$ for Dill EO and calculated values of E (%) by weigh loss method.

and dill essential oil. The plots are characterized by a single capacitive loop, corresponding to a charge transfer process. The size of the loop is enhanced by the concentration of the inhibitor. The difference in impedance between lower and higher frequencies is used to compute the transfer resistance values ($R_t$) [33]. The frequency (-$Z''_{\text{max}}$) at which the imaginary component of the impedance is maximal is given by Eq. (4) as well as the double layer capacitance ($C_{dl}$).
Wormwood and dill EOs are within the category of substances promised for industrial application in the field of corrosion of iron and steel in acidic conditions because they are stable goods that maintain their efficacy even at high temperatures.

**Thermodynamic parameters**

The Arrhenius relationship (6) [35] allows the activation energies without and with the inhibitor to be calculated by varying the logarithm of the corrosion rate as a function of absolute temperature (\( \ln(V_{corr}) = f(1/T) \)) (Fig. 3).

\[ W_{corr} = A^o \exp \left( - \frac{E_a^o}{RT} \right) \quad \text{and} \quad W_{corr} = A \exp \left( - \frac{E_a}{RT} \right) \]

where \( E_a \) and \( E_a^o \) are the energies of activation, respectively in the presence and absence of the inhibitor, \( A \) and \( A^o \) are constants, \( R \) is the universal constant of perfect gases, \( T \) is the absolute temperature in Kelvin and \( V_{corr} \) is the corrosion rate of the steel.

The values of the activation enthalpy \( \Delta H^o \) and entropy \( \Delta S^o \) can be calculated from the alternative transition relationship using the plot of the curves \( \ln(V/T) \) as a function of \( (1/T) \) in Fig. 4 [12]:

\[ W = \frac{RT}{Nh} \exp \left( \frac{\Delta S^o}{R} \right) \exp \left( - \frac{\Delta H^o}{RT} \right) \]

where \( N \) is the number of Avogadro, \( h \) is the Planck constant.

The thermodynamic parameters for the adsorption of the two investigated EOs onto mild steel in 1 M HCl are grouped in Table 6.

It is noted that the addition of the oils studied to the corrosive solution of 1 M hydrochloric acid, is accompanied by an increase in activation energy for wormwood EO. This increase shows that the mechanism of passage of the metal in solution has changed, this phenomenon also indicates that these EOs adsorb on the surface of the metal forming an electrostatic film [36]. The increase in activation energy can therefore be interpreted in terms of physisorption.

Dill EO has virtually no effect on activation energy. Similar results were found elsewhere Pennyroyal oil drift in acid solutions [27]. It is reasonable and highly probable that the adsorption of dill EO can be explained in terms of chemisorption.

<table>
<thead>
<tr>
<th></th>
<th>HCl 1M</th>
<th>Wormwood EO</th>
<th>Dill EO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_a^o ) (kJ.mol(^{-1}))</td>
<td>57</td>
<td>66</td>
<td>55</td>
</tr>
<tr>
<td>( \Delta H^o ) (kJ.mol(^{-1}))</td>
<td>55</td>
<td>64</td>
<td>53</td>
</tr>
<tr>
<td>( \Delta S^o ) (J.mol(^{-1}).K(^{-1}))</td>
<td>-67</td>
<td>-55</td>
<td>-82</td>
</tr>
</tbody>
</table>

![Fig. 3. Arrhenius curves of mild steel in 1M HCl without and with 2 g L\(^{-1}\) of wormwood EO (a) and dill EO (b).](image)
When wormwood EO is present, the thermodynamic activation parameters ($\Delta H^\circ$ and $\Delta S^\circ$) of the steel dissolution reaction in 1 M HCl are higher than they are in the solution without an inhibitor. The dissolution reaction is an endothermic one, as indicated by the positive value of the enthalpy $H^\circ$, and the dissolution of the steel is challenging [37]. The activation entropy $\Delta S^\circ$ is negative for the two investigated EOs, this shows that the newly formed activated complex is more ordered than the starting structure.

CONCLUSIONS

The electrochemical and gravimetric studies of the corrosion inhibition of steel in 1M HCl medium by two essential oils tested was carried out. The following conclusions can be drawn:

- The inhibition efficiency of both inhibitors increases with increasing concentration.
- The tested oils act as cathodic inhibitors.
- The proton is discharged according to pure activation kinetics.
- The addition of inhibitors changes the mechanism of proton reduction.
- Throughout the concentration range, the values of transfer resistance and double layer capacitance show an inverse trend.
- The results determined by the three well-known techniques weight loss - electrochemical curves - electrochemical impedance are in fairly good agreement.

- We infer that the carbon steel surface agrees with the Langmuir adsorption isotherm because it best fits the coverage surface and concentration. We estimated and discussed the thermodynamic activation parameters.

Acknowledgements

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