Nicotine as Corrosion Inhibitor for 1018 Steel in 1M HCl under Turbulent Conditions

Araceli Espinoza-Vázquez*, Sergio García-Galan and Francisco Javier Rodríguez-Gómez
Faculty of Chemistry, Department of Metallurgical Engineering, Universidad Nacional Autónoma de México, C.U., Distrito Federal, 04510, Mexico

Abstract
An electrochemical impedance technique for determining corrosion inhibition of nicotine in HCl on AISI 1018 steel under concentrations from 0 to 50 ppm found that the organic compound is a better corrosion inhibitor under static conditions. The inhibition efficiency (IE) increased with inhibitor concentration reaching an IE > 90%, at 10 ppm. For [nicotine] ≤ 50 ppm, the IE value reached 71%, at 40 rpm, but diminished then to 33% upon changing the concentration to 500 ppm. The hydrodynamic analysis showed a process ruled by physisorption according to the Langmuir adsorption model mechanism. Furthermore, the inhibition kinetics study showed that nicotine gave good protection against corrosion up to 72 hours of immersion with IE ≤ 87%. Finally, with increased temperature the IE values diminished from 90% at 25°C to 57% at 70°C, concluding that at high temperatures nicotine is ineffective at inhibition, because the temperature decrease, persistence layer easily desorbs.

Keywords: AISI 1018 steel; Nicotine; Corrosion inhibition

Introduction
The transport of hydrocarbons in the oil industry depends on the use of pipelines that can be damaged by corrosion, causing large impacts on production, significant damage to property, as well as pollution, and risk to human lives [1].

Corrosion inhibitors [2-5], such as molybdates, phosphates, and ethanolamines, are effective, but they are very toxic. The development of corrosion inhibitors, non-toxic and compatible with the environment, is an area of great importance in the science and technology of corrosion [6-8]. Inhibitor substances extracted from plants offer environmental and cost advantages; for example alkaloid extracts from Oxandra asbeckii plant [9], Hibiscus sabdariffa leaf [10], Geissospermum leaf [11] Euphorbia falcate [12] show 89% inhibition efficiency, Morinda tinctoria has a 70% at 30% v/v [13]; they have been tested, but there is a lack in assessing and identifying the active substance.

Nicotine ((S)-3-(1-methylpyrrolidin-2-il) pyridine) is an organic compound belonging to the alkaloids: a liquid, oily, and colorless derivative of the root nicotine, Figure 1, synthesized in the areas of high temperature the IE values diminished from 90% at 25°C to 57% at 70°C, concluding that at high temperatures nicotine is ineffective at inhibition, because the temperature decrease, persistence layer easily desorbs.

Consequently, our interest in evaluating this organic molecule as pure compound has been demonstrated inhibition properties against corrosion thus making it an eco-friendly material equally proper for engineering uses under different hydrodynamic conditions and temperatures, which simulates the transport of hydrocarbons.

The inhibition efficiency of nicotine, IE, can be calculated as [21]:

\[
IE / \% = \frac{1}{R_p} \text{ inhibitor} \times 100 (1)
\]

where \( R_p \) is the polarization resistance with ("inhibitor") or without inhibitor ("blank").

The value of polarization resistance is an important parameter that can be obtained from electrochemical impedance spectroscopy to estimate the rate of corrosion, by using small polarization, i.e., no damage on the electrode is caused due to experiment.

Materials and Methods

Inhibitor solution 0.01M nicotine (Alrich 97% purity) was prepared in water, with different aliquots taken from this solution, with concentrations ranging from 5 to 50 ppm added to the 1M HCl

*Corresponding author: Araceli Espinoza-Vázquez, Faculty of Chemistry, Department of Metallurgical Engineering, Universidad Nacional Autónoma de México, C.U., Distrito Federal, 04510, Mexico, Tel: 52-55-56225225; E-mail: arasv_21@yahoo.com.mx

Received August 26, 2015; Accepted September 30, 2015; Published October 07, 2015


Copyright: © 2015 Espinoza-Vázquez A, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
The electrochemical impedance study was performed at room temperature using the Gill AC workstation, applying a sinusoidal ± 10 mV perturbation, within the 10−3 Hz to 105 Hz frequency range to an electrochemical cell with a three-electrode setup. A saturated Ag / AgCl electrode was used as reference, with a graphite rod as counter electrode, while the working electrode (rotating cylinder electrode, RCE) was the AISI 1018 steel sample with ~ 3.92 cm2 exposed area, electrode, while the working electrode (rotating cylinder electrode, RCE) was the AISI 1018 steel sample with ~ 3.92 cm2 exposed area, electrolyte, prepared through dilution of the HCl analytical grade reagent at 37% with doubly distilled water.

The study under hydrodynamic conditions was carried out at 0, 40, 100 and 500 rpm. In addition, a study of kinetic inhibition of nicotine to establish steady-state open-circuit potential. Working electrode was first immersed into the test solution for 30 min with inhibitor concentration. Analysis of the shape of the Nyquist plots revealed the curves were approximated by two semicircles: one time-constant at low frequency associated with a corrosion process, while the second time-constant at low frequency would likely be associated with inhibitor adsorption [23,24].

When the RCE was at static condition (0 rpm) and at 10 ppm a Z_re decreases to 350 Ω·cm2 at 1000 Ω·cm2 at 50 ppm. On the other hand, at 100 rpm, Figure 2d, Z_re decreases to 350 Ω·cm2 at 50 ppm, attributable to the presence of electrodonor groups (pairs of free electrons in atoms in nitrogen) that favor the adsorption of nicotine on the metal surface.

For the description of a frequency-independent phase shift between an applied AC potential and its current response, a constant phase element (CPE) is used, which is defined in impedance representation as:

\[ Z_{CPE} = Y_0^{-1} (j\omega)^{-n} \]

where \( Y_0 \) is the CPE, or CPE, n is the CPE exponent that can be used as a gauge of the heterogeneity or roughness of the surface, j the unit imaginary number, and \( \omega \) is the angular frequency in rad/s. Depending on n, CPE can represent a resistance \( (Z_{CPE}=R, n=0) \), capacitance \( (Z_{CPE}=C, n=1) \), or inductance \( (Z_{CPE}=L, n=-1) \). The equation to convert \( Y_0 \) into double layer capacitance \( (C_{dl}) \) is given by ref. [26-28]:

\[ C_{dl} = Y_0 (\sigma_{ads})^{-1} \]

Tables 1-4 show the corresponding values from the simulation of the experimental data, demonstrating that in all cases the concentration has greater polarization resistance compared with non-inhibitor.

Results and Discussion

Effect of concentration

Figure 2a shows impedance diagrams for the immersed metal, with an increase in the value of Z_re at higher rotation rates in 1M HCl due to the increase of mass transfer and localized attack [22].

Figure 2b-2e show the results for different rotation rates; the diameters of semicircles in Nyquist plots increas with increasing the inhibitor concentration. Analysis of the shape of the Nyquist plots revealed the curves were approximated by two semicircles: one time-constant at high frequency associated with a corrosion process, while the second time-constant at low frequency would likely be associated with inhibitor adsorption [23,24].

When the RCE was at static condition (0 rpm) and at 10 ppm a Z_re decreases to 350 Ω·cm2 at 50 ppm. On the other hand, at 100 rpm, Figure 2d, Z_re decreases to 350 Ω·cm2 at 50 ppm, attributable to a desorption of organic molecules on the electrode surface [25].

To determine electrochemical parameters of nicotine for different rotation rates (static and turbulent flows), simulation using electrical circuits was carried out using the Zview program, which are shown in Figure 3. Electrical equivalent-circuit diagram in Figure 3a corresponds to the metal/solution interface (double layer between the metallic surface and acid solution). Figure 3b describes a two-time-constant model, corresponding to the metal/solution interface and the inhibitor adsorption. \( R_i \) is the solution resistance, \( R_{mol} \) the charge transfer resistance, \( R_{rot} \) the molecular resistance, CPE, and CPE, the constant phase elements corresponding to the R_mol and R_c, respectively.

The value of polarization resistance is calculated as:

\[ Z_{CPE} = Y_0^{-1} (j\omega)^{-n} \]

For the description of a frequency-independent phase shift between an applied AC potential and its current response, a constant phase element (CPE) is used, which is defined in impedance representation as:

\[ Z_{CPE} = Y_0^{-1} (j\omega)^{-n} \]

where \( Y_0 \) is the CPE, or CPE, n is the CPE exponent that can be used as a gauge of the heterogeneity or roughness of the surface, j the unit imaginary number, and \( \omega \) is the angular frequency in rad/s. Depending on n, CPE can represent a resistance \( (Z_{CPE}=R, n=0) \), capacitance \( (Z_{CPE}=C, n=1) \), or inductance \( (Z_{CPE}=L, n=-1) \). The equation to convert \( Y_0 \) into double layer capacitance \( (C_{dl}) \) is given by ref. [26-28]:

\[ C_{dl} = Y_0 (\sigma_{ads})^{-1} \]

For the description of a frequency-independent phase shift between an applied AC potential and its current response, a constant phase element (CPE) is used, which is defined in impedance representation as:

\[ Z_{CPE} = Y_0^{-1} (j\omega)^{-n} \]

where \( Y_0 \) is the CPE, or CPE, n is the CPE exponent that can be used as a gauge of the heterogeneity or roughness of the surface, j the unit imaginary number, and \( \omega \) is the angular frequency in rad/s. Depending on n, CPE can represent a resistance \( (Z_{CPE}=R, n=0) \), capacitance \( (Z_{CPE}=C, n=1) \), or inductance \( (Z_{CPE}=L, n=-1) \). The equation to convert \( Y_0 \) into double layer capacitance \( (C_{dl}) \) is given by ref. [26-28]:

\[ C_{dl} = Y_0 (\sigma_{ads})^{-1} \]

The results in Table 5 indicate that the process is physisorption (electrostatic interaction), since the value of \( \Delta G^o_{ads} \) obtained from the linear fit shown in Figure 5 is less than -20 kJ/mol for the four-rotation rates tested [36-39].

Strong correlation coefficient \((R^2 ≥ 0.9979)\) of the Langmuir adsorption isotherm for nicotine was observed. The Langmuir...
Figure 2: Nyquist diagrams at different concentrations of nicotine as a corrosion inhibitor at different rotation rates.
adsorption isotherm assumes that the adsorption of organic molecules on the adsorbent is a monolayer. The high values of the adsorption equilibrium constant reflect the high adsorption ability of the nicotine molecules on the steel surface.

**Effect of immersion time**

Corrosion inhibitors are often evaluated in order to determine their performance under different conditions, such as the concentration, but few evaluated for persistence of the layer inhibitor. It is important to study the effect of immersion time to optimize concentration [40,41].

In the Nyquist plot of Figure 6, some examples of impedance curves at three different immersion times in the presence of 50 ppm of nicotine in 1M HCl are shown, with 24 hours of immersion producing a maximum $Z_{re}$ value of 854 Ω·cm$^2$. After that time, this value decreases; at 240 hours it is remarkable to observe two time-constants, one attributed to the charge transfer resistance (corrosion process) and a second time-constant corresponding to an adsorbed molecular layer [42]. In Table 6, the values of corresponding resistances for each immersion time are summarized.

In order to clarify the behavior of nicotine (50 ppm) as a function of immersion time, Figure 7, a maximum inhibition period of 72 hours

---

**Table 1**: Electrochemical parameters of nicotine (0 rpm).

<table>
<thead>
<tr>
<th>C/ppm</th>
<th>Rs/Ω·cm$^2$</th>
<th>n</th>
<th>Cd/lµF·cm$^{-2}$</th>
<th>Rp/Ω·cm$^2$</th>
<th>IE/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.5</td>
<td>1.0</td>
<td>400.3</td>
<td>141.1</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>10.9</td>
<td>0.9</td>
<td>392.2</td>
<td>403.8</td>
<td>65.0</td>
</tr>
<tr>
<td>10</td>
<td>9.5</td>
<td>0.9</td>
<td>432.5</td>
<td>431.2</td>
<td>67.3</td>
</tr>
<tr>
<td>20</td>
<td>8.9</td>
<td>0.8</td>
<td>441.0</td>
<td>394.7</td>
<td>64.3</td>
</tr>
<tr>
<td>50</td>
<td>7.6</td>
<td>0.8</td>
<td>429.9</td>
<td>490.8</td>
<td>71.2</td>
</tr>
</tbody>
</table>

**Table 2**: Electrochemical parameters of nicotine/solution interface (40 rpm).

<table>
<thead>
<tr>
<th>C/ppm</th>
<th>Rs/Ω·cm$^2$</th>
<th>n</th>
<th>Cd/lµF·cm$^{-2}$</th>
<th>Rp/Ω·cm$^2$</th>
<th>IE/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.3</td>
<td>0.8</td>
<td>435.3</td>
<td>117.6</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>3.4</td>
<td>0.9</td>
<td>374.1</td>
<td>308.4</td>
<td>61.9</td>
</tr>
<tr>
<td>10</td>
<td>3.4</td>
<td>0.9</td>
<td>396.8</td>
<td>337.1</td>
<td>65.1</td>
</tr>
<tr>
<td>20</td>
<td>3.5</td>
<td>0.9</td>
<td>431.5</td>
<td>349.2</td>
<td>66.3</td>
</tr>
<tr>
<td>50</td>
<td>3.5</td>
<td>0.9</td>
<td>489.2</td>
<td>355.9</td>
<td>67.0</td>
</tr>
</tbody>
</table>

**Table 3**: Electrochemical parameters of nicotine/solution interface (100 rpm).

<table>
<thead>
<tr>
<th>C/ppm</th>
<th>Rs/Ω·cm$^2$</th>
<th>n</th>
<th>Cd/lµF·cm$^{-2}$</th>
<th>Rp/Ω·cm$^2$</th>
<th>IE/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.5</td>
<td>1.0</td>
<td>760.0</td>
<td>141.1</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>2.9</td>
<td>0.9</td>
<td>314.9</td>
<td>191.1</td>
<td>26.1</td>
</tr>
<tr>
<td>10</td>
<td>2.8</td>
<td>0.9</td>
<td>372.9</td>
<td>206.9</td>
<td>31.8</td>
</tr>
<tr>
<td>20</td>
<td>2.6</td>
<td>0.9</td>
<td>462.9</td>
<td>210.5</td>
<td>33.0</td>
</tr>
<tr>
<td>50</td>
<td>2.6</td>
<td>0.9</td>
<td>515.8</td>
<td>210.7</td>
<td>33.0</td>
</tr>
</tbody>
</table>

**Table 4**: Electrochemical parameters of nicotine/solution interface (500 rpm).

**Figure 3**: Equivalent electrical circuits.

**Table 5**: Thermodynamic analysis of nicotine at different rotation rate by the Langmuir adsorption model.

<table>
<thead>
<tr>
<th>Rotation rate/rpm</th>
<th>Ln $k_{ads}$</th>
<th>$\Delta G^0_{ads}$/kJ mol$^{-1}$</th>
<th>Regression Equation</th>
<th>Linear/mM</th>
<th>$R^2$ (correlation coefficient)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.77</td>
<td>-13.11</td>
<td>$C/\theta=1.0864 C+0.0031$</td>
<td>0.9999</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>4.16</td>
<td>-9.44</td>
<td>$C/\theta=1.3839 C+0.0156$</td>
<td>0.9797</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>5.13</td>
<td>-11.65</td>
<td>$C/\theta=1.4812 C+0.0059$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>3.61</td>
<td>-8.21</td>
<td>$C/\theta=2.9628 C+0.0269$</td>
<td>0.9795</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4**: Variation in the efficiency of inhibition by nicotine as the corrosion inhibitor in turbulent flow.

**Figure 5**: Adsorption isotherm of nicotine in 1M HCl on immersed 1018 steel at different rotation rates.
Effect of Temperature

It has been observed that temperature can modify the interaction between the metal and the inhibitor [43]. In Figure 8, Nyquist plots are shown corresponding to: a) steel immersed in 1M HCl, and b) steel immersed in 50 ppm nicotine in the corrosive medium, at different temperatures.

Figure 8a shows that the value of $Z_{re}$ decreases with increasing temperature, attributable to the 1M HCl solution causing material (steel) loss due to a faster corrosion process. When the inhibitor is added (50 ppm at Figure 8b), the previously mentioned effect in immersion time with temperature is also shown, with low charge transfer resistance at high temperature, as can be seen in Table 7. This fact is attributed to the inhibitor formed on the metal surface, thus a decrease in strength of the adsorption process at elevated temperature, suggesting physical adsorption [44] or desorption of the organic molecules (nicotine) at higher temperatures [45].

Conclusion

It was demonstrated that nicotine is an efficient corrosion inhibitor in HCl under static conditions, but only up to 10 ppm with efficiencies around –90%. However, turbulent flow conditions (>40 rpm) affected the corrosion inhibition with IE less than 70%.

The nicotine is adsorbed on the metallic surface consistent with the Langmuir isotherm model.

The inhibitors behavior is affected with increase in temperature decreasing the persistence of the layer due to desorption process; according to the ASTM G 170 standard, this inhibitor is not suitable for high temperatures.
According to the ASTM G48 or G78 standard, the inhibitor is accepted when there is persistence of a test layer after 72 hours immersion. The inhibitors for this research meet that criterion.

Acknowledgements

The authors are grateful to the Faculty of Chemistry (UNAM), Department of Metallurgy and DGAPA for a postdoctoral fellowship for the corresponding author. AEV and FJRG wish to acknowledge the SNI (Sistema Nacional de Investigadores) for the honor of membership and the stipends received.

References


