Corrosion inhibition of stainless steel N304 by dihydroxy benzyl phosphonic acid in 0.5 M H_2SO_4: Experimental and theoretical studies

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Dihydroxy benzyl phosphonic acid (DPA) has been studied as inhibitor against stainless steel N304 in 0.5 M sulfuric acid solution using the potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The inhibition efficiency was found to vary with the concentration of the inhibitor and elongating the immersion time. Electrochemical impedance spectroscopy (EIS) measurements confirmed the polarization data. The adsorption of (DPA) on the stainless steel N304 surface follow Langmuir adsorption isotherm. The results of quantum chemical calculations and experimental efficiencies of inhibitor were subjected to correlation analysis.

Keywords: Corrosion inhibition, Phosphonic acid, Electrochemical studies, Density functional theory, N304

The corrosion control by inhibitors is one of the most commun, effective and economic methods to protect metals in acid media1 most of well known acid corrosion inhibitors are organic compounds containing nitrogen, sulfur or oxygen atoms2,3, that can be adsorbed on the metal surface. A large number of these compounds are toxic in nature this has led to development of non toxic or relatively less toxic. Among these compounds, Organophosphorus compounds attracted a lot of attention. These compounds represent a very important class of compounds having a great activity in several fields such as agriculture, medicine and chemical4. Among these, phosphonic acids attracted a lot of attention.

Phosphonic acids, which are originally introduced as scale inhibitors, in water treatment, were later proved to be good corrosion inhibitors also. Their impact on the environment was reported to be negligible at the concentration levels used for corrosion inhibition5,6.

The objective of the present work is to investigate the inhibition effects of the (4-Dihydroxy Benzyl) Phosphonic Acid (DPA) on stainless steel N304 in 0.5 M sulfuric acid solution, using potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS) methods. Also, this study aims to use the Density Functional Theory method (DFT) to calculate the quantum chemical parameters in order to interpretate and predicate of experimental and theoretical reactivity of the studied inhibitor.

Experimental Section

Specimen and solution preparation

As discussed above, the material used for corrosion testing was N304 austenitic stainless steel. It was applied as a disk with an exposed surface area of 0.2 cm², the chemical composition of the steel is given in Table 1. The specimen was polished in first with a series of emery papers from 400, 600, 1000 and finally 4000 grade and then degreased with methanol and finally washed thoroughly with distilled water.

All measurements were carried out in 0.5 M H_2SO_4 (98% H_2SO_4 Sigma-Aldrich) solution in the absence and presence of various concentrations of inhibitor for all studies at room temperature. The inhibitor concentration range was from 1.10⁻⁶ to 1.10⁻³ M in H_2SO_4 solution, at 25°C. The molecular structure of dihydroxy benzyl phosphonic acid is given in Fig. 1.

Electrochemical measurement

The Electrochemical Measurement techniques, namely DC-Tafel slope and AC-Electrochemical impedance Spectroscopy (EIS), were used to study the corrosion behavior. All experiments were performed using a PGZ 301 Volta lab 40 system. The working electrode was first immersed into the test
solution for 30 min to establish a steady state open circuit potential. Polarization curves were obtained by changing the electrode potential automatically from -800 to -200 mV with a scan rate of 0.5 mV/s. The electrochemical impedance spectroscopy (EIS) measurements are carried at open circuit potential in a frequency range from 100 KHz to 10 MHz with amplitude of 10 mV. Experiments are repeated three times to ensure the reproducibility. Cyclic voltammetry was carried out for metal electrode and inhibitor covered electrode in the test solution. The working electrode was scanned from negative to positive values in the potential range of 0.85 V/SCE to 1.6 V/SCE at a scan rate of 25 mV/s.

Theoretical studies
Quantum chemical calculation were performed with total geometry optimizations applying Gaussian 09 program parcel the results were visualized by means of Gauss View 5.0.8 computer software with the RB3LYP /6-31G (d,p) by DFT method. Theoretical parameters such, the energies of the highest occupied and lowest unoccupied molecular orbital (E_HOMO and E_LUMO), energy gap ΔEgap (E_LUMO - E_HOMO ) and the dipole moment (μ) were determined.

Results and Discussion
Cyclic voltammetric study
Figure 2 shows the cyclic voltammogram of stainless steel in H2SO4 0.5M with 1×10⁻³ M of DPA solution, at 25°C. The cyclic voltamogramms shows an anodic peak at 0.01V attributed to oxidation of the metal. The cyclic voltamogramms of stainless steel in H2SO4 0.5M with 1×10⁻³ M of DPA do not show any oxidation or reduction, this suggests that DPA contributes to the protection of the metal corrosion.

Table 1 — Chemical composition of stainless steel N304.
<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt(%)</td>
<td>0.08</td>
<td>2.00</td>
<td>0.75</td>
<td>18.00</td>
<td>0.045</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Fig. 1 — Molecular structure of dihydroxy benzyl phosphonic acid (DPA)

Potendynamic polarization curves
Influence of the inhibitor concentration
Figure 3 shows the influence of DPA concentration on the anodic and cathodic potentiodynamic curves of stainless steel electrode in 0.5M H2SO4 solution containing different concentrations of DPA at 25°C.

Electrochemical parameters such corrosion densities (i_corr), corrosion potential (E_corr), the cathodic Tafel slope (β_c), the anodic Tafel slope (β_a) and the corrosion rate (τ) are collected in Table 2. The inhibition efficiency was evaluated from the measured i_corr values using the relationship:

\[ E(\%) = \left( \frac{i^0_{corr} - i_{corr}}{i_{corr}} \right) \times 100 \]

where i^0_corr and i_corr are the corrosion current densities values without and with inhibitor, respectively.

Fig. 2 — Cyclic voltammogram for stainless steel in H2SO4 0.5 M with 1.10⁻³ M of DPA.

Fig. 3 — Tafel polarization curves for stainless steel in 0.5 M H2SO4 at various concentrations of DPA.
Inspection of polarization curves and electrochemical parameters reveals that the corrosion rate decrease in the presence of DPA in acidic media. On the other hand, a compound is usually classified as an anodic of a cathodic type when the change in \( E_{corr} \) value is < 85 mV, after the addition of DPA, suggesting that the inhibitor acted as mixed type inhibitor. The corrosion rate of stainless steel reduced in the maximum value is obtained for \( 1 \times 10^{-3} \) DPA is 90.97% at 25°C.

Figure 4 shows the corrosion current density (\( I_{corr} \)) values of steel with different concentrations of the investigated inhibitor in 0.5 M H\(_2\)SO\(_4\) solution.

In acidic media, corrosion current density (\( I_{corr} \)) decreases noticeably with an increase in inhibitor concentration. It is clear that, the corrosion inhibition enhances with increasing the inhibitor concentration. This behavior is due to the fact that, the adsorption amount and coverage of inhibitor on steel surface increases with the inhibitor concentrations\(^1\).

**Effect of immersion period**

To study the influence of immersion period of stainless steel in 0.5 M H\(_2\)SO\(_4\) solution, the same technique (Potendynamic Polarization) was used the curves is shown in Fig. 5. By the addition of \( 1 \times 10^{-3} \) M of DPA in 0.5M H\(_2\)SO\(_4\) solution, it was found that corrosion rate decrease noticeably and the inhibition efficiency increases with immersion period. Variation of IE % versus immersion period of stainless steel 0.5 M H\(_2\)SO\(_4\) is given in Fig. 6. It is noteworthy that the inhibition efficiency attains 92.45% since 24 h at 25°C, the increase of IE% with immersion time as shown in Table 3 promises also the use of even during a long period.

**Electrochemical Impedance Spectroscopy (EIS)**

Figure 7 shows Nyquist plots for stainless steel in 0.5 M H\(_2\)SO\(_4\) solution with and without addition of various concentrations of DPA at 25°C. The inhibition efficiency obtained from the charge transfer resistance is calculated by:

\[
E(\%) = \left( \frac{R_{inh} - R}{R_{inh}} \right) \times 100
\]  \( \ldots (2) \)

\( R \) and \( R_{inh} \) are the charge transfer-resistance values with and without inhibitor, respectively. Table 4 summaries the impedance parameters from these studies, namely, charge transfer resistance (\( R \)) and double layer capacitance (\( C_d \)).

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>( E_{corr} ) (mv)</th>
<th>( I_{corr} ) (μA/cm(^2))</th>
<th>( \beta_a ) (mv)</th>
<th>( \beta_c ) (mv)</th>
<th>( R_p(\Omega.cm^2) )</th>
<th>( \tau (\mu m/Y) )</th>
<th>IE%((I_{corr}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-497.6</td>
<td>33.175</td>
<td>94.1</td>
<td>92.7</td>
<td>0.44</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( 10^{-6} )</td>
<td>-468.3</td>
<td>10.288</td>
<td>96.6</td>
<td>100.9</td>
<td>1.53</td>
<td>120.3</td>
<td>68.98</td>
</tr>
<tr>
<td>( 10^{-5} )</td>
<td>-471.6</td>
<td>7.725</td>
<td>89.8</td>
<td>94.0</td>
<td>1.92</td>
<td>90.35</td>
<td>76.71</td>
</tr>
<tr>
<td>( 10^{-4} )</td>
<td>-462.1</td>
<td>4.200</td>
<td>68.6</td>
<td>72.0</td>
<td>2.72</td>
<td>49.12</td>
<td>87.33</td>
</tr>
<tr>
<td>( 10^{-3} )</td>
<td>-452.7</td>
<td>3.055</td>
<td>62.4</td>
<td>69.1</td>
<td>4.93</td>
<td>35.73</td>
<td>90.79</td>
</tr>
</tbody>
</table>

Fig. 4 — Corrosion current density (\( I_{corr} \)) values for stainless steel in 0.5 M H\(_2\)SO\(_4\) at various concentrations of DPA

Fig. 5 — Variation of corrosion rate versus immersion time for stainless steel in 0.5 M H\(_2\)SO\(_4\) at various concentrations of DPA
It is apparent from these plots that the impedance in all cases corresponds to a capacitive loop. The semicircle diameters depend on the DPA concentration and increase with increasing of the latter. This indicates that the impedance of inhibited substrate increases with increasing inhibitor concentrations and consequently the inhibition efficiency increases.

However, the addition of inhibitor improves $R_t$ values and brings down $C_{dl}$ values. These observations clearly bring out the fact that the corrosion of stainless steel in 0.5 M H$_2$SO$_4$ is controlled by a charge transfer process and the corrosion inhibition occurs through the adsorption of DPA on stainless steel surface. Decrease in the $C_{dl}$ values, with can result from a decrease in local dielectric constant and/or an increase in courant density, the thickness of the electrical double layer, suggested that the DPA molecules function by adsorption at the metal-solution interface.

The equivalent circuit used to fit the EIS data of stainless steel in 0.5 M H$_2$SO$_4$ at various concentrations of DPA is shown in Figure 8.

Figure 9 Show the evolution of inhibition efficiency IE% as a function of the inhibitor concentration (acid) obtained from both electrochemical impedance measurements (EIS) and Tafel data. The impedance data confirm the inhibition behavior of the inhibitor with that obtained from tafel technique. it can be concluded that the inhibition efficiency found from polarisation curves and electorochemical impedance spectoscopy measurements are in good agreement.

### Adsorption isotherm

Adsorption isotherms are very important in determining the mechanism of organo electrochemical reaction. To study the interaction between inhibitor and the electrode surface we used isotherm of Langmuir.

The plots of $C_{inh}/\theta$ against $C_{inh}$ for the inhibitor at 25°C were straight lines as given in Figure 10. The correlation between $\theta$ and inhibitor concentration in the corrosive medium is given by the equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

... (3)

where, $\theta$ is the degree of coverage for different concentration of inhibitor molecules in 0.5 M H$_2$SO$_4$ solution using the the equation:

$$\theta = \frac{IE(\%)}{100}$$

... (4)

$C$ is the molar concentration of inhibitor, $K_{ads}$ is the related to the standard Gibbs free energy of adsorption. The values of the standard Gibbs free energy of adsorption are determined from the following equation:

$$C_{inh} = \frac{1}{K_{ads}} + C_{inh}$$

... (3)

Table 3 — Inhibition efficiencies of stainless steel obtained in 0.5 M H$_2$SO$_4$ at various concentrations of DPA with immersion time.

<table>
<thead>
<tr>
<th>Immersion time (h)</th>
<th>0</th>
<th>0.027</th>
<th>0.083</th>
<th>1</th>
<th>1.30</th>
<th>2</th>
<th>3</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau$ (µm/Y)</td>
<td>388.0</td>
<td>80.08</td>
<td>69.53</td>
<td>51.34</td>
<td>47.40</td>
<td>44.33</td>
<td>28.47</td>
<td>9.075</td>
</tr>
<tr>
<td>IE%</td>
<td>-</td>
<td>33.43</td>
<td>42.20</td>
<td>57.32</td>
<td>60.59</td>
<td>63.15</td>
<td>77.16</td>
<td>92.45</td>
</tr>
</tbody>
</table>
energy ($\Delta G_{ads}^0$) are calculated using the following equation\(^\text{10}\), where 55.5 is the molar concentration of water in the solution, R is the gas constant (8.314 K\(^{-1}\).mol\(^{-1}\)) and T is the absolute temperature (K).

$$K_{ads} = \frac{1}{5.55} e^{\left[\frac{\Delta G_{ads}^0}{RT}\right]} \quad \text{...(5)}$$

In literature, the standard free energy values around \(-20\) KJ mol\(^{-1}\) or lower are associated with an electrostatic interaction between the charged molecules and charged metal (physisorption), whereas those more negative than \(-40\) KJ mol\(^{-1}\) involve charge sharing or transfer from inhibitor molecules to metal surface to form a coordinate covalent bond (chemisorption)\(^\text{13,14}\). Commonly, high values of $K_{ads}$ indicate that, the inhibitor is simply and strongly adsorbed on the metal surface, leading to a better inhibition performance\(^\text{14}\). From Table 5, the obtained value of $\Delta G_{ads}^0$ by the two methods were -39.93 KJ/mol ($K = 1.816.10^5$) by the use of Tafel slopes and -37.781KJ/mol ($K = 7.614.10^4$) according to the EIS measurement, revealing that both physical adsorption and chemical adsorption\(^\text{13,14}\).

In order to demonstrate the high inhibition rate of the studied inhibitors, we made comparisons between our results and the results reported in previous studies for same types of compounds\(^\text{11,15,16}\) (Table 6).

### Theoretical studies

Quantum chemical calculations were performed to explain the relationship between the molecular structure and the inhibitive action of the inhibitors under study\(^\text{17}\). Geometry optimizations and quantum chemical calculations were carried out on the studied DAP using the RB3LYP /6-31G (d,p) model. The optimized structure, $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ of the inhibitors are shown in Figure 11. Quantum chemical parameters including the energy gap ($\Delta E$) between HOMO and LUMO, and the molecular dipole ($\mu$) were determined and summarized in Table 5.
HOMO and LUMO are very important for describing the chemical reactivity, where HOMO represents the ability to donate an electron, whereas (although) LUMO have no electrons represent the ability to obtain an electron. Higher values of $E_{\text{HOMO}}$ indicate better inhibitory activity with increased adsorption of the inhibitor on the metal surface, whereas the low value of $E_{\text{LUMO}}$ indicates the ability to accept the electron of the molecule\textsuperscript{18}, therefore, the increase of $E_{\text{HOMO}}$ and a decadence of $E_{\text{LUMO}}$ increases the adsorption capacity of the inhibitor.

The energy gap $\Delta E_{\text{gap}}$ ($E_{\text{LUMO}} - E_{\text{HOMO}}$) is the energy between the frontiers orbital; it is an important parameter to describe the reactivity of the inhibitor molecule towards the metal surface. As $\Delta E_{\text{gap}}$ decreases this imply that the polarization and the adsorption of the molecule on the metal surface is much easy, however the reactivity of the molecule increases leading to better inhibition efficiency\textsuperscript{19,20}.

The dipole moment ($\mu$) is the electronic parameter that reflects the polarity of the molecule; it is the result from the distribution non-uniform of charges of various atoms in the molecule. The inhibitor with a high dipole moment has the ability to form strong dipole-dipole interactions with the metal surface, which results in high surface adsorption and thus greater inhibition efficiency\textsuperscript{21}. In the present study, the dipole moment of DPA is 2.0445 Debye, this results indicates the strong adsorption of the molecule at the stainless steel surface.

**Conclusion**

The corrosion inhibition of stainless steel in 0.5 M $\text{H}_2\text{SO}_4$ solution by Dihydroxy benzyl phosphonic acid has been studied by potentiodynamic polarization curves and electrochemical impedance spectroscopy.
The DPA emerge as very good inhibitors against stainless steel in 0.5M H₂SO₄ medium and inhibition efficiency follows the order 90.97% to 1×10⁻³M and the corrosion rate decreases with increase in concentration of the inhibitor.

Potentiodynamic polarization measurements showed that the DPA acts as mixed-type inhibitor. EIS measurements also indicate that the inhibitor increases the charge transfer resistance and show that the inhibitive performance depends on adsorption of the molecules on the metal surface.

The inhibition efficiencies determined by impedance spectroscopy measurements (EIS) techniques increases with DPA concentration and its highest value (86.68%) at 1×10⁻³M concentration.

The adsorption of DPA mechanism obeys the Langmuir isotherm at 25°C and the negative values of AG⁰ads indicate spontaneous adsorption of the inhibitor on the surface of stainless steel.

Quantum chemical results of DPA showed higher value of E_HOMO, lower value of E_LUMO, and smaller value of ΔE in the same time the inhibition efficiency increases indicating that the DPA is a good corrosion inhibitor for stainless steel N304 in sulfuric acid.

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References