

Corrosion inhibition of stainless steel N304 by dihydroxy benzyl phosphonic acid in 0.5 M H₂SO₄: 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 common, 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 atoms^{2,3}, 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 inhibition^{5,6}.

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 H₂SO₄ (98% H₂SO₄ 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 H₂SO₄ 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 0.5mV/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 10mV. 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 method¹⁵. Theoretical parameters such, the energies of the highest occupied and lowest unoccupied molecular orbital (E_{HOMO} and E_{LUMO}), energy gap ΔE_{gap} ($E_{LUMO} - E_{HOMO}$) and the dipole moment (μ) were determined.

Results and Discussion

Cyclic voltammetric study

Figure 2 shows the cyclic voltammogram of stainless steel in H_2SO_4 0.5M with 1×10^{-3} M of DPA solution, at 25°C. The cyclic voltammograms shows an anodic peak at 0.01V attributed to oxidation of the metal⁷. The cyclic voltammograms of stainless steel in H_2SO_4 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.

Table1 — Chemical composition of stainless steel N304.

Element	C	Mn	Si	Ni	P	S
Wt(%)	0.08	2.00	0.75	18.00	0.045	0.30

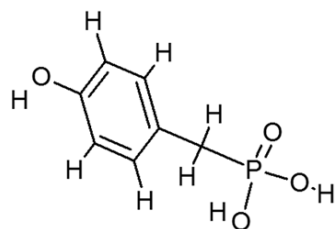


Fig. 1 — Molecular structure of dihydroxy benzyl phosphonic acid (DPA)

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 H_2SO_4 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 relationship⁸.

$$E(\%) = \frac{(i_{corr}^0 - i_{corr})}{i_{corr}^0} \times 100 \quad \dots (1)$$

where i_{corr}^0 and i_{corr} are the corrosion current densities values without and with inhibitor, respectively.

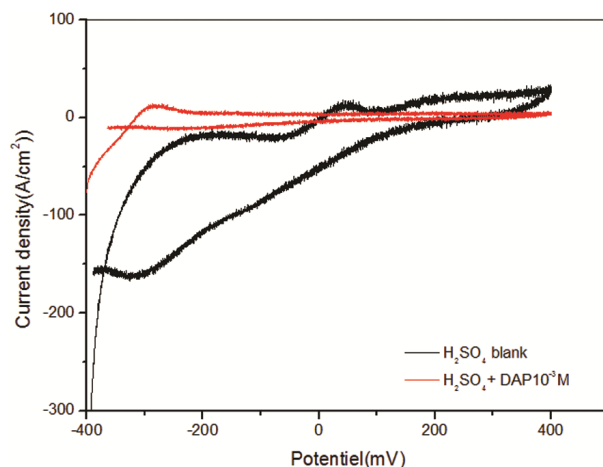


Fig. 2 — Cyclic voltammogram for stainless steel in H_2SO_4 0.5 M with 1.10^{-3} M of DPA.

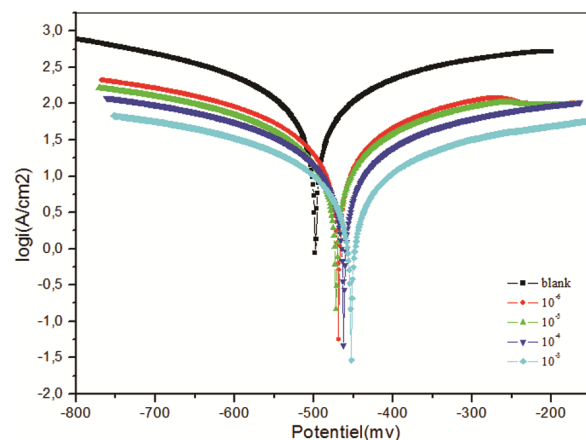


Fig. 3 — Tafel polarization curves for stainless steel in 0.5 M H_2SO_4 at various concentrations of DPA.

Table 2 — Polarization parameters and corresponding efficiency for the stainless steel in 0.5 M H₂SO₄ at various concentrations of DPA

Concentration (M)	E _{corr} (mv)	I _{corr} (μA/cm ²)	β _a (mv)	- β _c (mv)	R _p (Ω.cm ²)	τ (μm/Y)	IE%(I _{corr})
Blank	-497.6	33.175	94.1	92.7	0.44	388.0	-
10 ⁻⁶	-468.3	10.288	96.6	100.9	1.53	120.3	68.98
10 ⁻⁵	-471.6	7.725	89.8	94.0	1.92	90.35	76.71
10 ⁻⁴	-462.1	4.200	68.6	72.0	2.72	49.12	87.33
10 ⁻³	-452.7	3.055	62.4	69.1	4.93	35.73	90.79

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 or a cathodic type when the change in E_{corr} value is < 85 mV⁹, 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 1×10⁻³ DPA is 90.97% at 25°C.

Figure 4 show the corrosion current density (I_{corr}) values of steel with different concentrations of the investigated inhibitor in 0.5 M H₂SO₄ solution.

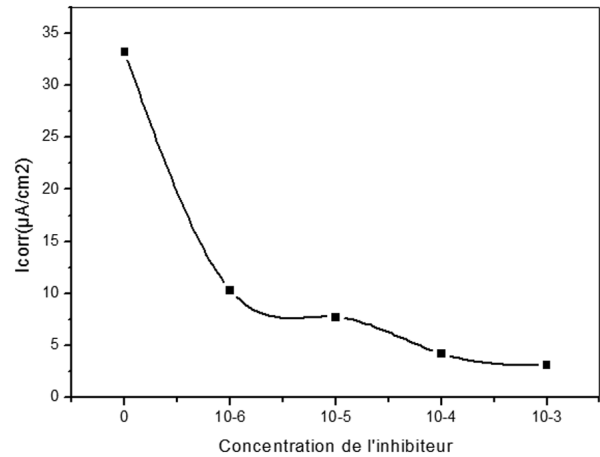
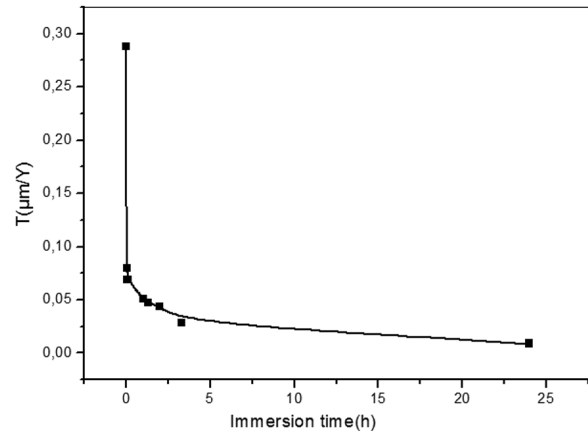
In acidic media, corrosion current density (I_{corr}) decreases noticeably with an increase in inhibitor concentration. It is clear that, the corrosion inhibition enhances with increasing the inhibitor concentration. This behavior is due to the fact that, the adsorption amount and coverage of inhibitor on steel surface increases with the inhibitor concentrations¹⁰.

Effect of immersion period

To study the influence of immersion period of stainless steel in 0.5 M H₂SO₄ solution, the same technique (Potendynamic Polarization) was used the curves is shown in Fig. 5. By the addition of 1×10⁻³ M of DPA in 0.5M H₂SO₄ solution, it was found that corrosion rate decrease noticeably and the inhibition efficiency increases with immersion period. Variation of IE % versus immersion of stainless steel 0.5 M H₂SO₄ 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 show Nyquist plots for stainless steel in 0.5 M H₂SO₄ 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:


 Fig. 4 — Corrosion current density (I_{corr}) values for stainless steel in 0.5 M H₂SO₄ at various concentrations of DPA

 Fig. 5 — Variation of corrosion rate versus immersion time for stainless steel in 0.5 M H₂SO₄ at various concentrations of DPA

$$E(\%) = \frac{(R_{inh} - R_t)}{R_{inh}} \times 100 \quad \dots (2)$$

R_t 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_t) and double layer capacitance (C_{dl}).

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 it 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

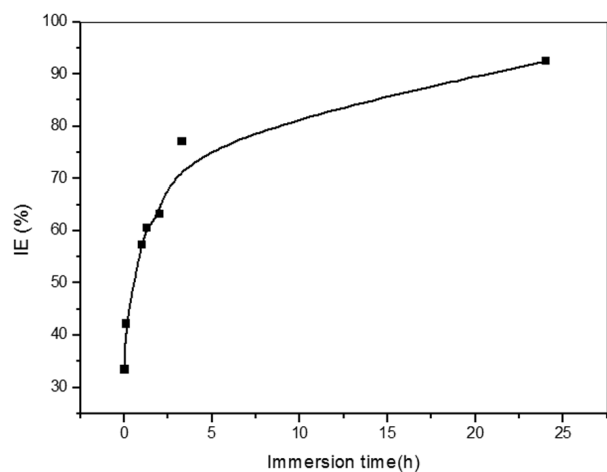


Fig. 6 — Variation of IE% versus immersion time for stainless steel in 0.5 M H₂SO₄ at various concentrations of DPA

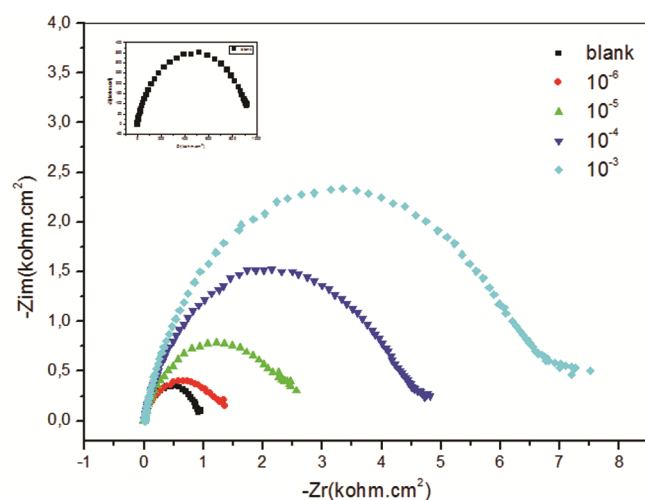


Fig. 7 — Nyquist impedance diagrams for stainless steel in 0.5 M H₂SO₄ at various concentrations of DPA

steel in 0.5 M H₂SO₄ 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 interface¹¹.

The equivalent circuit used to fit the EIS data of stainless steel in 0.5 M H₂SO₄ 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 electrochemical impedance spectroscopy measurements are in good agreement.

Adsorption isotherm

Adsorption isotherms are very important in determining the mechanism of organo electrochemical reaction¹². To study the interaction between inhibitor and the electrode surface we used isotherm of Langmuir.

The plots of C_{inh}/θ against C_{inh} for the inhibitor at 25°C were straight lines as given in Figure 10. The correlation between θ and inhibitor concentration in the corrosive medium is given by the equation¹⁰.

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad \dots (3)$$

where, θ is the degree of coverage for different concentration of inhibitor molecules in 0.5 M H₂SO₄ solution using the the equation¹⁰.

$$\theta = \frac{IE(\%)}{100} \quad \dots (4)$$

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

Table 3 — Inhibition efficiencies of stainless steel obtained in 0.5 M H₂SO₄ at various concentrations of DPA with immersion time.

Immersion time (h)	0	0.027	0.083	1	1.30	2	3	24
τ ($\mu\text{m}/\text{Y}$)	388.0	80.08	69.53	51.34	47.40	44.33	28.47	9.075
IE%	-	33.43	42.20	57.32	60.59	63.15	77.16	92.45

Table 4 — Electrochemical impedance parameters for stainless steel in 0.5 M H₂SO₄ at various concentrations of DPA

Concentration (M)	R _s (Ω. cm ²)	R _i (Ω. cm ²)	C _{dl} (μF. cm ²)	θ	IE(%)
Blank	1.719	0.952	33.42	-	-
10 ⁻⁶	4.81	1.371	46.40	0.30	30.56
10 ⁻⁵	9.77	2.666	39.67	0.64	64.29
10 ⁻⁴	5.95	4.629	8.594	0.79	79.43
10 ⁻³	23.5	7.151	7.922	0.86	86.68

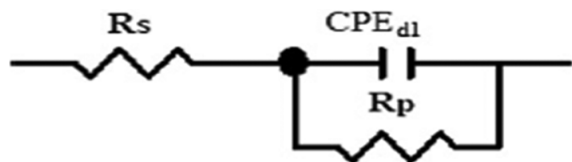
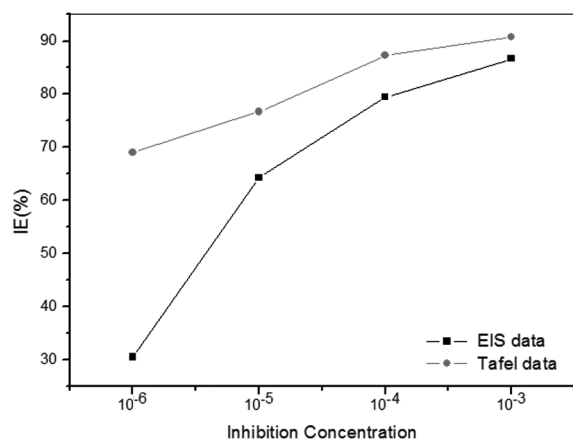


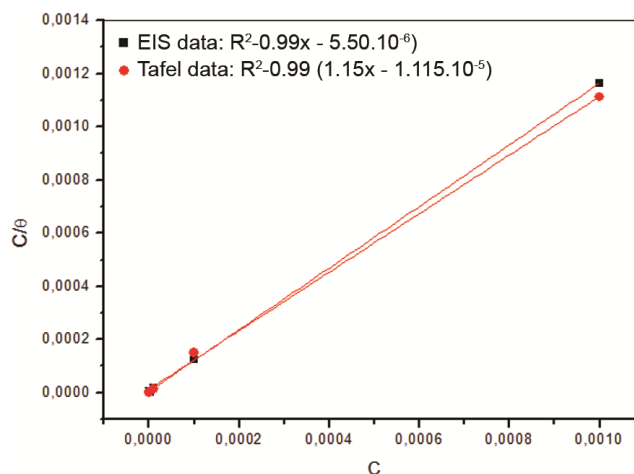
Fig. 8 — Equivalent circuit used for modeling metal/solution interface in the absence and presence of DPA


 Fig. 9 — Variation of inhibition efficiency of stainless steel obtained by Tafel data and EIS in 0.5 M H₂SO₄ of DPA.

energy (ΔG_{ads}^0) are calculated using the following equation¹⁰, 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).

$$K_{ads} = \frac{1}{5.55} \cdot e^{\left(\frac{\Delta G_{ads}^0}{RT}\right)} \quad \dots(5)$$

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)^{13,14}. Commonly, high values of K_{ads}


 Fig. 10 — Langmuir adsorption isotherm model for the stainless steel in 0.5 M H₂SO₄ obtained by Tafel and EIS data

indicate that, the inhibitor is simply and strongly adsorbed on the metal surface, leading to a better inhibition performance¹⁴. From Table 5, the obtained value of ΔG_{ads}^0 by the two methods were -39.93 KJ/mol ($K = 1.816 \cdot 10^5$) by the use of Tafel slopes and -37.781KJ/mol ($K = 7.614 \cdot 10^4$) according to the EIS measurement, revealing that both physical adsorption and chemical adsorption^{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^{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 study¹⁷. 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_{HOMO} and E_{LUMO} of the inhibitors are shown in Figure 11. Quantum chemical parameters including the energy gap (ΔE) between HOMO and LUMO, and the molecular dipole (μ) were determined and summarized in Table 5.

Table 5 — Quantum chemical parameter of DPA

Quantum parameters	E_{tot} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_{gap} (eV)	μ (debye)
DPA	-24884.8617	-5.9231	-0.1153	5.8105	2.0445

Table 6 — Comparison of results obtained in this study by previous works of similar type of compounds.

Structure	Present inhibitor	Laamari et al. ^[11]	Inhibition Efficiency Labjar et al. ^[15]	Prabakaran et al. ^[16]
IE %	90.79	73.24	69.22	69.00

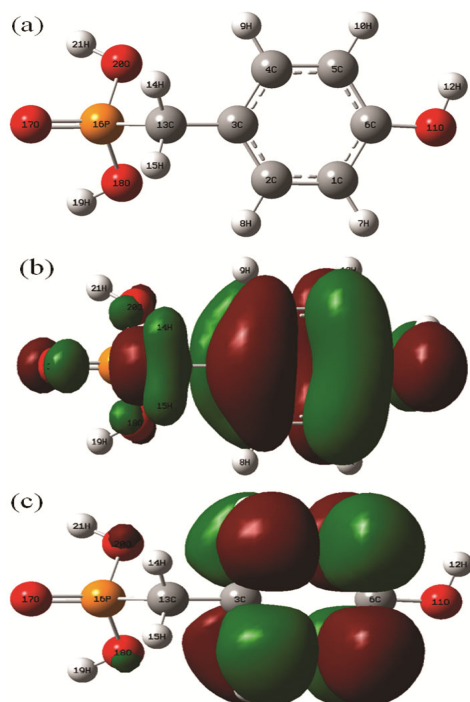


Fig. 11 — The optimized structure (left) and HOMO (center) and LUMO (right) distribution for molecules DPA. [Atom legend: white = H; grey = C; red = O; Orange = P].

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. HOMO and LUMO are very important for describing the chemical reactivity, where HOMO represents the ability to donate an electron, whereas LUMO represents the ability to

obtain an electron. Higher values of E_{HOMO} indicate better inhibitory activity with increased adsorption of the inhibitor on the metal surface, whereas the low value of E_{LUMO} indicates the ability to accept the electron of the molecule¹⁸, therefore, the increase of E_{HOMO} and a decrease of E_{LUMO} increases the adsorption capacity of the inhibitor.

The energy gap ΔE_{gap} ($E_{LUMO} - E_{HOMO}$) 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 ΔE_{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^{19,20}.

The dipole moment (μ) 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 efficiency²¹. 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 H_2SO_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 ΔG°_{ads} 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.

Acknowledgement

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