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The Penicillin Derivatives as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution: Experimental and Theoretical Studies

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The inhibition performances of four penicillin derivatives, including penicillin G, oxacillin, penicillin V and amoxicillin as organic corrosion inhibitors for mild steel in 1.0 M HCl solution were investigated by weight loss measurement and Tafel polarization technique. The electrochemical results reveal that the four penicillin derivatives are qualified, mix-type corrosion inhibitors, and the inhibition efficiency follow the order: oxacillin>amoxicillin>penicillin V>penicillin G. The results obtained from electrochemical and weight loss studies are in reasonable agreement. Quantum chemical calculation was used to correlate inhibition abilities with their electronic structural parameters. In addition, the molecular dynamics simulations were employed to get insight into the equilibrium adsorption configurations and calculate the binding energy between the inhibitors and iron surface. Theoretical calculations support the experimental results and elucidate working mechanisms.

Keywords: penicillin derivatives, Tafel polarization, quantum chemistry, molecular dynamic simulation

1. INTRODUCTION

Mild steel is a well-known host material and used in industrial engineering to undertake the tasks of transportation of water, petroleum products and chemicals. However, it is susceptible towards corrosion, especially in circumstance of acid pickling, aiming at removal of scales or rusts and thus provision clean surface for pre-passivating treatment.[1-3] The corrosion of mild steel is of fundamental

academic and industrial concern, and efficient corrosion preventitives are highly desirable and will reduce economic loss, avoid potential disasters, protect underground water and eliminate negative social impacts. Among a multitude of corrosion prevention schemes, corrosion inhibitors have been regarded as the most promising measurement to retard the metal dissolution process owning to the advantages of high efficiency and strong practicability.[4-6] Compared with the toxic inorganic corrosion inhibitors, well-designed organic corrosion inhibitors, which always contain π electrons or heteroatoms, like phosphorus, nitrogen, sulphur, and oxygen in molecule structure, are easily to meet the essential requirements for corrosion inhibitors, such as environmental green, low effective dosage and high efficiency, and have attracted considerable interests.[7-10] Unfortunately, the complicated synthetic procedures lead to high operating costs.

In recent years, some research groups have poured attention to utilization of drugs as organic corrosion inhibitors for various metals and alloys in acid media.[11-16] Their experimental results demonstrated that most of the selected drugs were found to exhibit satisfactory corrosion inhibitive performances. Through careful analysis of the representative drugs, the existence of the multi-heterocycles and the common conjugated π-bonds facilitate the adsorption process of drugs on metal surface and thus formation the protective molecular film to block active sites and inhibit the corrosion destruction. It is certainly that from the economic point of view, the prices of drugs are more expensive than commercial corrosion inhibitors. However, the employment of expired or useless drugs will transform trash into treasure. Gece published the review article concerning the 17 categories of drugs used as metallic corrosion inhibitors under different corrosive environments.[17] Penicillin derivatives containing *β*-lactam group are widely used as antibacterial agents and regarded as the potential candidates for corrosion inhibition due to their mature production process, relative low toxicity to environment and suitable molecular structure.[18,19] However, a survey of literatures reveals that little information is provided on their working mechanisms in detail.

Theoretical calculation chemistry has been applied to explain the mechanism of corrosion inhibitor. Quantum chemistry using density functional theory (DFT) has been proved to successfully correlate the corrosion inhibition efficiency with the molecular/electronic properties of organic molecules.[20-22] Molecular dynamic (MD) simulation is very powerful tool for analyzing adsorption process and offer the valuable information, including equilibrium adsorption configuration, binding energy between organic corrosion inhibitor and metal surface, etc.[23-26] Undoubtedly, theoretical calculations as necessary supplementation can provide specific insights into the mechanism of inhibition action at the molecular level and guide the research and development of a new generation of organic corrosion inhibitors. Herein, in order to elucidate the influence of molecular structure on inhibition efficiency, the four penicillin derivatives, penicillin G, oxacillin, penicillin V, and amoxicillin as alternative corrosion inhibitors for mild steel in 1.0 M HCl solution were studied using weight loss measurement and Tafel polarization technique. Quantum chemical calculations were further performed, and various quantum chemical indices were calculated and correlated with the inhibitive effect. Finally, the adsorption of penicillin derivatives on Fe (110) was studied by MD simulations.

2. EXPERIMENTAL SECTION

2.1. Materials

The mild steel specimens are of the following composition (wt%): C: 0.17, Si: 0.46, Mn: 0.46, P: 0.05, S: 0.017, Cr: 0.08, Cu: 0.19 and the balance Fe. The specimens were meticulously prepared prior all experimental procedures. They were polished with different grades of emery papers (from #600 to #1500), and then washed with ethanol, acetone, consequently rinsed by double distilled water and dried under room temperature. The aggressive medium for the study was prepared form reagent grade HCl and double distilled water. The four penicillin derivatives were purchased from Aldrich Chemical Co., Inc. and their chemical structures are given in Figure 1.

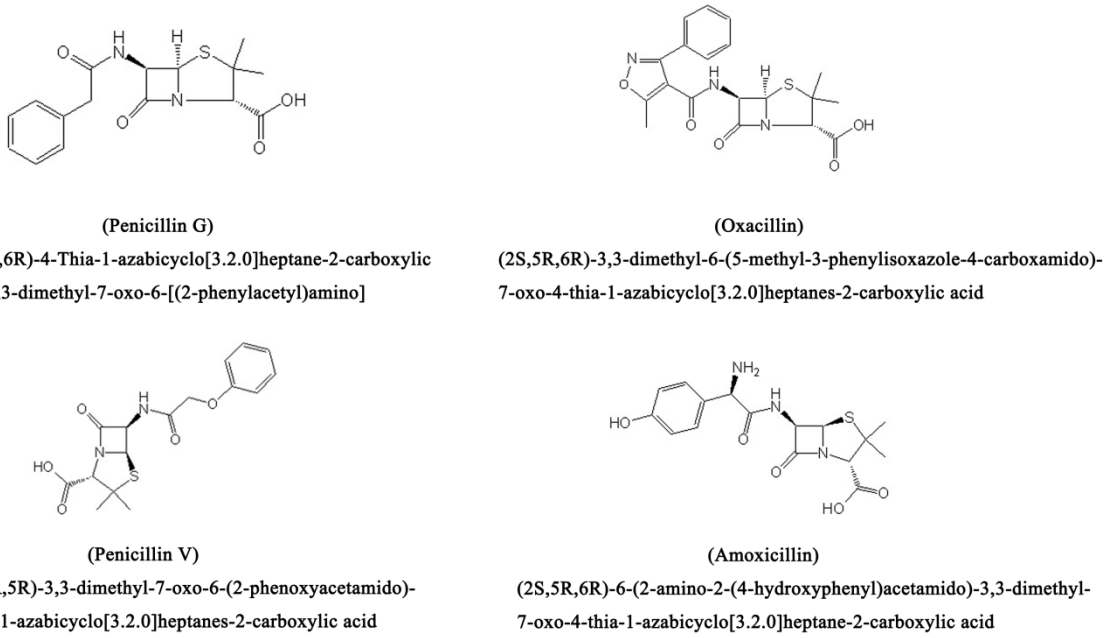

Figure 1. The chemical structures of the four penicillin derivatives.

2.2. Weight loss measurements

The pre-weighted mild steel specimens (2.5 cm × 2 cm × 0.025cm) were immersed in the beakers containing 250 mL of 1.0 M HCl with and without different concentrations of the tested inhibitors at 25 ℃ under aerated conditions for 24 h. After that, the specimens were withdrawn, scrubbed with bristle brush, rinsed with double distilled water and acetone, dried under room temperature, and weighted accurately. The gravimetric experiments were carried out in triplicates to obtain good reproducibility. The corrosion rate (C_R), surface coverage (θ) and inhibition efficiency (η_{WL}, %) were calculated from the following Equations:

$$C_R = \frac{W_0 - W_i}{ST} \quad (1)$$

$$\theta = \frac{W_0 - W_i}{W_0} \quad (2)$$

$$\eta_{WL}\% = \frac{W_0 - W_i}{W_0} \times 100 \qquad (3)$$

Where W_0 and W_i are the average weight loss of three parallel mild steel specimens in absence and presence of inhibitors, respectively, S is the total area per cm^2 and T is the immersion time as 24 h.

2.3. Tafel polarization measurements

Electrochemical studies were performed on the Parastat 2273 system (Princeton Applied Research) facilitated with a conventional three-electrode electrochemical cell. The mild steel specimens were embedded in a Tafel holder with an exposed area of 0.5 cm^2 and used as the working electrode, a platinum sheet with 1.0 cm^2 surface area and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The working electrode was first immersed in the test solution for 30 min to attain a steady-state open-circuit potential (OCP). The Tafel polarization curves obtained in the potential ranged from -250 to +250 mV with a sweep rate of 0.166 mV sec^{-1}. Each experiment was done at room temperature without any stirring.

2.4. Quantum chemistry calculation and molecular dynamic simulation

Quantum chemical calculations were conducted with Gaussian 03 program. All electron calculations of inhibitor molecules were accomplished using the functional hybrid B3LYP density function theory (DFT), which is considered to be a standard method for modeling many chemical process, formalism with electron basis set 6-31G(d, p) for all atoms to produce highly accurate results of the molecular structure. Geometry optimizations were performed with no symmetry constraints, Frequency calculation was executed simultaneously, and no imaginary frequency was found, confirming the minimum-energy structures. The following quantum chemical parameters, the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy band gap ($\Delta E=E_{LUMO}-E_{HOMO}$), dipole moment ($D$), electronegativity ($\chi$), global hardness ($\eta$) and the fraction of were electrons transferred from the inhibitor to the metallic surface (ΔN), calculated from the obtained optimized molecular structure.

The MD simulations were performed using the Discover program with COMPASS (condensed phase optimized molecular potentials for atomistic simulation studies) force field in Material Studio 4.0 software from Accelrys Inc. The surface Fe (110) was chosen for the simulation study due to its stable property. Interaction between the inhibitors and the Fe (110) surface were carried out in a simulation box (29 Å × 29 Å × 67 Å) with periodic boundary conditions to simulate a representative part of an interface devoid of any arbitrary boundary effects. The energy optimized inhibitor molecule, Fe (110) surface and water layers were constructed using the amorphous cell module. The MD simulation was performed under 298 K, NVT ensemble, with a time step of 0.1 fs and simulation time of 1000 ps. During the process of simulations, all the atoms in Fe (110) surface were fixed. The interaction energy ($E_{Fe\text{-}inhibitor}$) between Fe (110) surface and the inhibitor molecule was calculated according to the following equation:

$$E_{\text{Fe-inhibitor}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{inhibitor}}) \quad (4)$$

where E_{total} is the total energy of the iron crystal together with the adsorbed inhibitor molecule, E_{surface} and $E_{\text{inhibitor}}$ are the total energy of the iron crystal and free inhibitor molecule, respectively. The binding energy of the inhibitor molecule is the negative value of the interaction energy, namely

$$E_{\text{binding}} = -E_{\text{Fe-inhibitor}} \quad (5)$$

3. RESULTS AND DISCUSSION

3.1. Weight loss measurement

The inhibitive effect of penicillin derivatives addition at different concentrations on the mild steel corrosion in 1.0 M HCl at 25 ℃ was investigated by weight loss measurements. The obtained corrosion rate (C_R), the surface coverage (θ) and the inhibition efficiency (η_{WL}, %) are shown in Table 1. It is clear that penicillin derivatives retard the dissolution of mild steel. The C_R values of mild steel decrease, and meanwhile the η_{WL} values increase as increasing concentrations of the four inhibitors in 1.0 M HCl solution. At 1.0 mM concentration, penicillin G, oxacillin, penicillin V and amoxicillin exhibit maximum η_{WL} as 75.4 %, 93.1 %, 79.6 %, and 90.6 %, respectively, which represent satisfactory inhibition abilities. This behaviour can be attributed to the adsorption and the coverage of the studied inhibitors on mild steel surface. Comparing the η_{WL} values at all concentrations, the inhibition efficiency of the four penicillin derivatives decreases in the following order: oxacillin> amoxicillin>penicillin V>penicillin G.

Table 1. Corrosion rates of mild steel in 1.0 M HCl and inhibition efficiency for different concentrations of the penicillin derivatives from weight loss measurements.

inhibitor	Conc. (mM)	C_R (mg m^{-2} h^{-1})	η_{WL} (%)	θ
Blank	-	2.5	-	-
Penicillin G	0.01	1.83	18.5	0.185
	0.05	1.15	46.3	0.463
	0.1	0.77	69.2	0.692
	1.0	0.58	75.4	0.754
Oxacillin	0.01	1.06	59.8	0.598
	0.05	0.63	78.3	0.783
	0.1	0.41	92.2	0.922
	1.0	0.4	93.1	0.931
Penicillin V	0.01	1.75	22.3	0.223
	0.05	1.03	57.4	0.574
	0.1	0.61	74.2	0.742
	1.0	0.51	79.6	0.796
Amoxicillin	0.01	1.45	40.3	0.403
	0.05	0.76	68.9	0.689
	0.1	0.48	75.6	0.756
	1.0	0.43	90.6	0.906

3.2. Tafel polarization measurement

Tafel polarization measurements have been applied to investigate the mechanisms and kinetics of anodic and cathodic reactions occurring in the metal surface. The Tafel polarization curves for mild steel in the absence and presence of the four penicillin derivatives in 1.0 M HCl are shown in Figure. 2. The electrochemical parameters including corrosion current density (I_{corr}), cathodic and anodic Tafel slopes (β_c and β_a), which were obtained by extrapolating the linear Tafel segments, corrosion potential (E_{corr}), and the inhibition efficiency (η_{Tafel}, %) are given in Table 2. The inhibition efficiency was calculated by using the following equation.

$$\eta_{\text{Tafel}},\% = (1-\frac{I_{corr,0}}{I_{corr}})\times 100 \qquad (6)$$

Where $I_{corr,0}$ and I_{corr} are the corrosion current densities of the mild steel immersed in 1.0 M solution with and without corrosion inhibitors, respectively.

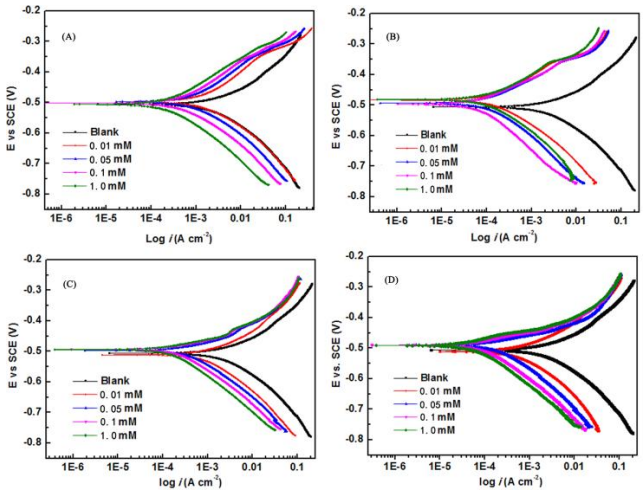

Figure 2. Tafel polarization curves for mild steel in 1.0 M HCl without and with different concentrations of inhibitors at 25 ℃: (A) penicillin G, (B) oxacillin, (C) penicillin V, and (D) amoxicillin.

Through careful analysis of these data, several conclusions can be drawn as following:

(1) After the addition of any penicillin derivative, both anodic and cathodic Tafel polarization curves shift towards lower current density. As increasing the concentration of corrosion inhibitors, the I_{corr} values decrease significantly and the η_{Tafel} values increase obviously, implying the formation of protective film on the mild steel surface.

(2) For all the penicillin derivatives, the presence of the corrosion inhibitors shifts E_{corr} values slightly compared to the uninhibited curve (blank), the largest displacement of E_{corr} observed at concentration of 5×10^{-2} mmol L^{-1} for oxacillin is 24.1 mV, which is far lower than the 85 mV. Generally speaking, if the displacement in corrosion potential is more than 85 mV with respect to corrosion potential of the blank, the inhibitor can be regarded as cathodic or anodic type.[27,28] Furthermore, there is no regular change in the slopes of the cathodic/anodic Tafel lines by changing the

inhibitors concentrations, which are also reflected in the relatively stable values of β_c and β_a with respect to the blank. Therefore, in summary, the four penicillin derivatives are the mix-type corrosion inhibitors by blocking mechanism on the available metallic active sites to decrease the corrosion rates. It is worthwhile to note that they do not change the reaction kinetics of the iron dissolution and the hydrogen evolution.

(3) Comparing the η_{Tafel} values of the four penicillin derivatives under different concentrations, it is not difficult to summarize that the corrosion inhibition efficiency of the four inhibitors decreases in the following sequences: oxacillin>amoxicillin> penicillin V>penicillin G, which are in a good agreement with the weight loss results. From the view of molecular structure, oxacillin seems to have the most reactive sites, which is the main reason for the best inhibiting performance among the four penicillin derivatives.

Table 2. Tafel Polarization parameters for the corrosion mild steel in 1.0 M HCl solution containing different concentrations of penicillin derivatives at 25 ℃

Inhibitor	Conc. (mM)	I_{corr} (μA cm^{-2})	E_{corr} (mV)	β_C (mV dec^{-1})	β_a (mV dec^{-1})	η_{Tafel} (%)
Blank	-	1767	-505.4	117.5	58.4	-
Penicillin G	0.01	1236	-496.8	121.6	59.2	30.1
	0.05	755	-497.9	125.5	57.8	57.3
	0.1	512	-501.3	122.9	58.9	71.0
	1.0	457	-505.7	131.4	57.2	74.1
Oxacillin	0.01	555	-482.7	135.9	61.5	68.6
	0.05	317	-481.3	144.6	60.4	82.1
	0.1	121	-493.4	139.5	58.7	93.1
	1.0	119	-497.7	149.2	62.4	93.2
Penicillin V	0.01	944	-511.0	121.1	59.1	46.6
	0.05	617	-496.9	127.8	60.4	65.1
	0.1	465	-492.8	131.9	59.8	73.7
	1.0	399	-494.0	124.6	61.2	77.4
Amoxicillin	0.01	559	-510.9	137.8	63.4	68.4
	0.05	443	-490.9	125.9	63.9	74.9
	0.1	314	-490.2	121.2	62.7	82.2
	1.0	197	-491.3	124.9	59.9	88.9

3.3. Quantum chemical calculation methods

Quantum chemical calculations have been used to predict the inhibition performance of corrosion inhibitors, which can quantitatively investigate the relationship between inhibition efficiency and spatial molecular structure as well as molecular electronic structure by analysis of the calculated quantum parameters. It is well known that the phenomenon of metal corrosion appears in aqueous phase, in order to calculate more precisely, the quantum chemical calculations were carried out in water phase using a polarized continuum model (PCM). The optimized geometries of the four penicillin derivatives including their HOMO and LUMO distribution density are shown in Figure 3

and the calculated parameters such as E_{HOMO}, E_{LUMO}, ΔE, dipole moment (D), χ, η and ΔE of these inhibitors are given in Table 3. It can be observed that from Figure 3 that the HOMO of oxacillin is mainly distribution in the azabicyclo moiety, while the LUMO is concentrated in the phenylisoxazole moiety. As for penicillin G, the HOMO and LUMO were all located on the azabicyclo moiety. Penicillin V and amoxicillin have the similar distributions of HOMO and LUMO, the HOMO orbitals are entirely on the phenyl moiety, in the case of LUMO orbitals, the distribution are mainly on the azabicyclo moiety.

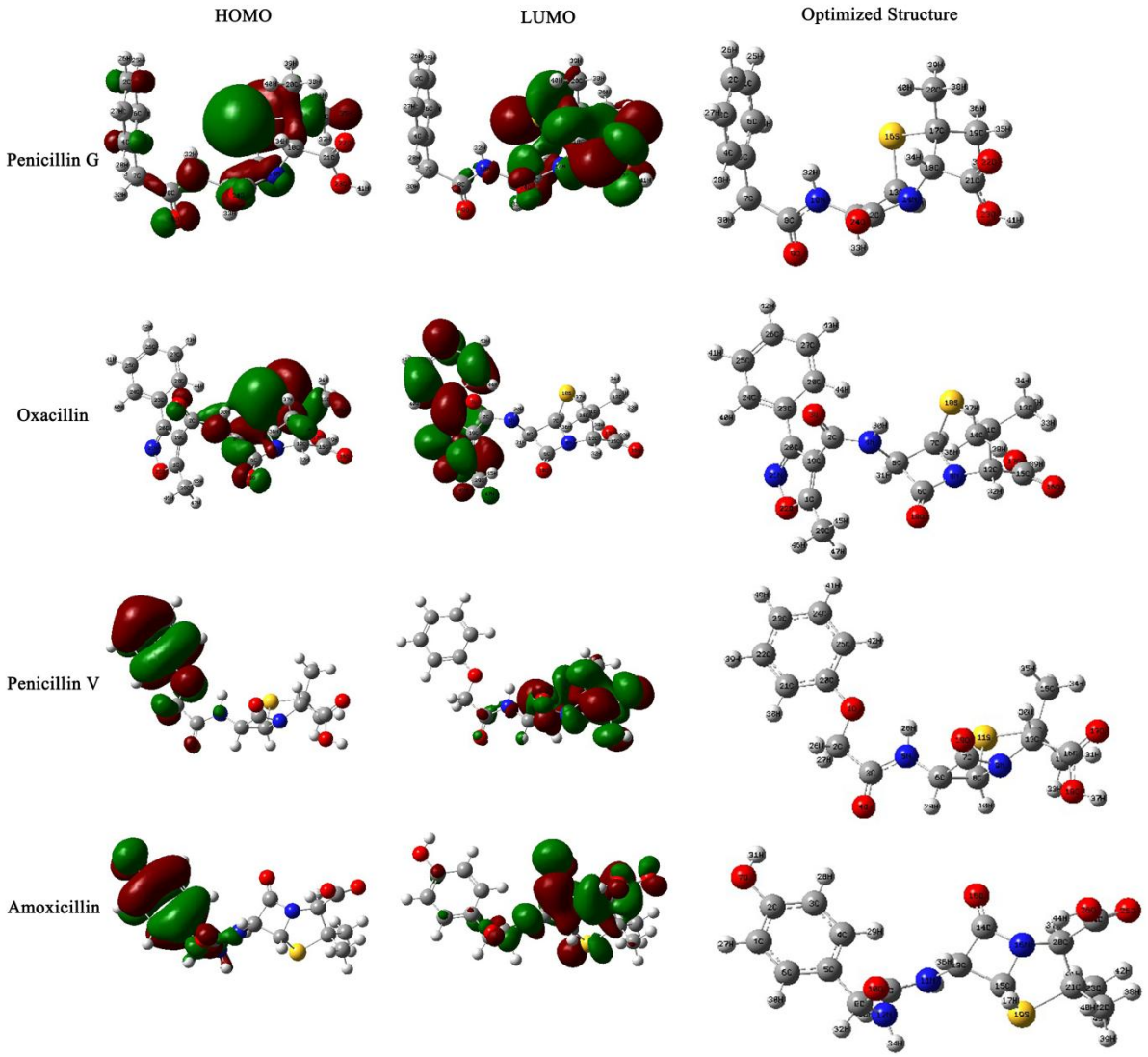

Figure 3. The optimized geometry, HOMO, and LUMO orbitals of penicillin G, oxacillin, penicillin V and amoxicillin in aqueous phase.

According to the frontier molecular orbital theory, the formation of a transition state is attributed to an interaction between HOMO and LUMO orbitals of reacting species. E_{HOMO} indicates the tendency of an organic molecule to donate electrons. The higher values of E_{HOMO} are, the stronger the electron donating abilities of the molecules are. E_{LUMO} suggests the propensity of a molecule to

accept electrons. The lower values of E_{LUMO}, the more probable it is that the molecule accept electrons. From Table 3, the value of E_{HOMO} obviously increases in the order of penicillin G <oxacillin<penicillin V<amoxicillin. Unfortunately, this theoretical result is not in agreement with the experimental result of inhibition efficiency. However, at the same time, the values of E_{LUMO} follow the order: penicillin G>penicillin V>amoxicillin≈ oxacillin, which is basically accordant with the experimental results. That is to say, the ability of acceptance electrons from metal surface basically obeys the order of inhibition efficiency. More importantly, ΔE, the energy gap between HOMO and LUMO, is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on metallic surface. A corrosion inhibitor molecule with low ΔE value is generally associated with high chemical reactivity, facilitates adsorption process and thus favours good inhibition efficiency. As indicated in Table 3, the value of ΔE follows the order oxacillin<amoxicillin<penicillin V<penicillin G, which is completely compatible with the experimentally determined inhibition efficiency, suggesting that the inhibition efficiency is dependent on integrated abilities of electrons donated to unoccupied orbitals of the metal and free electrons accepted from the metal surface. The dipole moments of penicillin G, oxacillin, penicillin V and amoxicillin are 5.99, 7.06, 5.24 and 6.50 D, respectively, which are all more than that of water with standard value of 1.85 D, suggesting that all the penicillin derivatives own the ability to displace molecules from the mild steel surface and thereby inhibit the corrosion of steel against corrosive medium. The previously literatures about the relationship between diploe moments and inhibition efficiency still remains controversial and there are no apparent relevancy in this work. It is noteworthy that oxacillin possessing the biggest value of dipole moment and molecular volume, which maybe realize the maximum coverage on metal surface. This is also the important reason behind the best corrosion inhibition efficiency.

Table 3. The calculated quantum parameters for penicillin G, oxacillin, penicillin V, and amoxicillin in aqueous phase.

Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta E = E_{LUMO} - E_{HOMO}$ (eV)	dipole (D)	molecular volume ($cm^3\ mol^{-1}$)	χ (eV)	η (eV)	ΔN
Penicillin G	-6.884	-1.034	5.85	5.99	234.5	3.959	2.925	0.519
Oxacillin	-6.83	-1.524	5.306	7.06	270.1	4.177	2.653	0.532
Penicillin V	-6.558	-1.034	5.524	5.24	251.7	3.796	2.762	0.580
amoxicillin	-6.476	-1.143	5.333	6.50	231.9	3.810	2.666	0.598

Additionally, the energies of HOMO and LUMO orbital of inhibitor molecule are related to the ionization potential (I) and the electron affinity (A), respectively, given by the following equations:

$$I = -E_{HOMO} \quad (7)$$

$$A = -E_{LUMO} \quad (8)$$

Absolute electronegativity, χ, and absolute hardness, η of iron and inhibitor molecule are given by the following equations:

$$\chi = \frac{I + A}{2} \qquad (9)$$

$$\eta = \frac{I - A}{2} \qquad (10)$$

The number of electrons transferred from the inhibitor to metallic surface (ΔN) is calculated depending on the quantum chemical method:

$$\Delta N = \frac{\chi_{\mathrm{Fe}} - \chi_{\mathrm{inh}}}{2(\eta_{\mathrm{Fe}} + \eta_{\mathrm{inh}})} \qquad (11)$$

Where a theoretical value of χ_{Fe}=7 eV is taken for iron and η=0 is assumed, since I=A for bulk metals.

As listed in Table 3, the phenomena of ΔN>0 for all inhibitors demonstrate that the electrons can transfer from the molecules to metal surface, favouring the formation of adsorptive bonds. According to Lukovits et al.,[29,30] the inhibition efficiency increases with increasing electron-donating ability of the molecule at the metals surface if ΔN<3.6. It can be concluded from Table 3 that all the values are less than 3.6, and the order is amoxicillin>penicillin V>oxacillin>penicillin G, which is different from the sequence of the inhibition efficiency. However, after investigating the results of the frontier orbital energies, it can be inferred that for the penicillin derivatives, the difference in inhibition efficiency should mainly be attributed to the difference ability of acceptance of electrons from mild steel surface.

The molecular reactivity of the studied inhibitors has been evaluated from the analyses of global molecular reactivity. But this is not sufficient to estimate the particular active atoms of inhibitor molecules. Undoubtedly, corrosion inhibitor molecules adsorb on metal surface by the electron transferring process. Therefore, it is essential to distinguish the active sites accounting for donating or accepting electrons. Fukui indices are commonly used to analyse the behaviour of the different sites within the organic corrosion inhibitors. They provide entire information about the reactive centres and condense the values around each atomic site into a single value that characterize nucleophilic and electrophilic nature. The Fukui function f_{k} is defined as the first derivative of the electronic density $\rho(\vec{r})$ with respect to the number of electrons N in a constant external potential $v(\vec{r})$:

$$f_{\mathrm{k}} = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{v(\vec{r})} \qquad (12)$$

For the electron-transfer controlled reaction, Fukui functions inform about the sites in a molecule on which nucleophilic, electrophilic are most possible. In the present work, the condensed Fukui functions are calculated by applying finite difference approximation:

$$f_{\mathrm{k}}^{+} = q_{\mathrm{k}}(N+1) - q_{\mathrm{k}}(N) \text{ (for nucleophilic attack)} \qquad (13)$$

$$f_{\mathrm{k}}^{-} = q_{\mathrm{k}}(N) - q_{\mathrm{k}}(N-1) \text{ (for electrophilic attack)} \qquad (14)$$

Where q_{k}(N+1), q_{k}(N), q_{k}(N-1) represent the net charge of atom k in a molecule with N+1, N, and N-1 electrons, respectively. f_{k}^{+} and f_{k}^{-} represent the nucleophilic attacking index and the electrophilic attacking index, respectively.

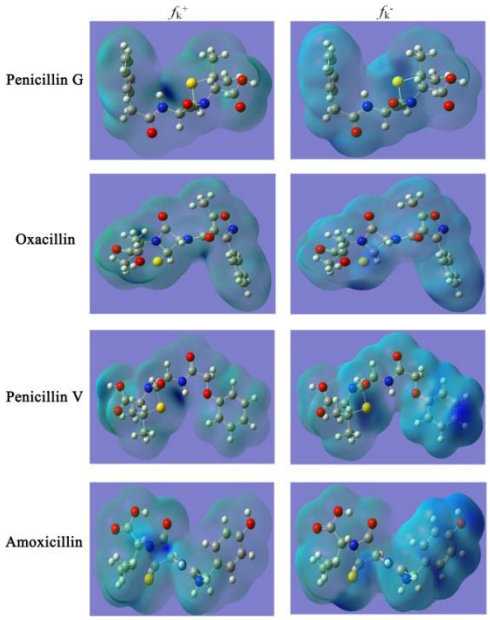

Figure 4. The Fukui functions for penicillin G, oxacillin, penicillin V amoxicillin calculated by DFT.

Table 4. Fukui indices of penicillin G, oxacillin, penicillin V and amoxicillin.

Inhibitor	Atom	f_k^+	Atom	f_k^-
Penicillin G	C1	0.498	C2	0.104
	C3	0.287	O9	0.119
	C8	0.282	S16	0.198
	C12	0.376	C19	0.128
	S16	0.247		
Oxacillin	C5	0.378	S10	0.156
	C6	0.134	C13	0.99
	S10	0.240	C14	0.101
	C11	0.190	C26	0.106
	C15	0.125	N21	0.145
Penicillin V	C6	0.328	S11	0.154
	S11	0.366	C23	0.124
	C15	0.123		
	C16	0.149		
Amoxicillin	C1	0.113	C1	0.102
	C3	0.272	C3	0.112
	C8	0.387	O7	0.130
	C13	0.290	S19	0.164
	O18	0.1		
	C15	0.259		
	S19	0.168		
	C20	0.765		

The calculated Fukui indices for the four penicillin derivatives are presented in Table 4. Generally speaking, the preferred sites for nucleophilic attacks are the atoms where the value of f_k^+ is

the highest, while the preferred sits for electrophilic attack are the atom in the molecule where f_k^- has the highest value. It can be seen in Table 4 that C1, C3, C8, C12, S16 in penicillin G; C5, C6, S10, C11, C15in oxacillin; C6, S11, C15, C16 in penicillin V and C1, C3, C8, C13, O18, C15, S19, C20 in amoxicillin atoms with high f_k^+ values are responsible for nucleophilic attack. On the other hand, atoms C2, O9, S16, C19 in penicillin G, S10, C13, C14, C26 in oxacillin, S11, C23 in penicillin V and C1, C3, O7 S19 in amoxicillin are the most probable centres for electrophilic attacks due to their relatively high f_k^- values. Figure 4 shows the Fukui function distributions in the four penicillin derivatives. Combined with the distributions of HOMO and LUMO, the distributions of Fukui function match the results of the surfaces of the inhibitors. The function f_k^+ is associated with the LUMO and measures reactivity toward a donor species and the function f_k^- is associated with the HOMO and measures reactivity toward an acceptor species. It is possible to observe from Figure 4 that all the penicillin derivatives have many actives for adsorption on mild steel surface. By comparison, except for the core structure of azabicyclo group, the existence of phenylisoxazole substituents make the more adsorption centres in oxacillin, which may be the reason for the highest inhibitive performance among the four corrosion inhibitors.

3.4. Molecular dynamics (MD) simulations

To better understand the adsorption behaviour between the four penicillin derivatives and the mild steel surface in aqueous phase, MD simulations were performed. Previously studies have proved that MD simulation can precisely predict the most favourable configuration of an inhibitor on the metal surface under various environments. In the present work, during MD simulation, when the temperature and energy of the systems reach the equilibrium state, $E_{\text{Fe-inhibitor}}$ and E_{binding}, the important parameters to evaluate the inhibition efficiency, are obtained and tabulated in Table 5.

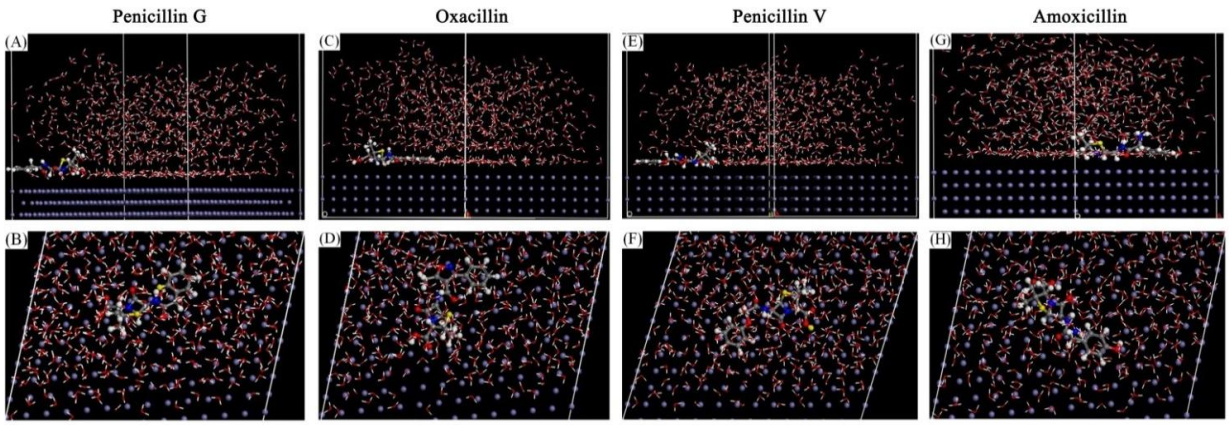

Figure 5. Equilibrium configurations for adsorption of penicillin G (A, B), oxacillin (C, D), penicillin V (E, F) and amoxicillin (G, H).

The final equilibrium configurations of the corrosion inhibitors are depicted in Figure 5. It is clearly observed that all the inhibitors displace the water molecule and adsorb onto Fe (110) surface in

nearly parallel mode. These equilibrium configurations ensure that as many as possible adsorption centres contact with Fe (110) surface and the coordination or feedback bonding between the inhibitor molecules and Fe (110) surface are easily formed. There is no doubt that these adsorption configurations will maximize the contact area per molecule and thus achieve the maximum coverage on metal surface. After distinguishing the configurations, the majority of reactive atoms with nucleophilic or electrophilic tendencies are close to Fe (110) surface. The atoms with high f_k^- values can offer electrons to the unoccupied d orbital of iron to form coordinate bonds, while the atoms with high fk+ can also accept the electrons from d orbital of iron to form feedback bonds, consequently forming the protective film and preventing Fe (110) surface from aggressive species attack. In the above discussion, the sulphur atoms in all the penicillin derivatives show the high reactive abilities. However, in the equilibrium configurations, the distances between sulphur atoms and Fe (110) surface are not the minimum. It is conceivable that the molecular torsion balance is the main reason responsible for these phenomena and molecular torsions result in the fact that the azabicyclo group cannot completely parallel to Fe (110) surface during the adsorption process.

The negative values of $E_{\text{Fe-inhibitor}}$ (shown in Table 5) indicate the adsorption processes are spontaneous. Furthermore, comparing the E_{binding} values, the order is penicillin G<penicillin V< amoxicillin<oxacillin, which is in keeping with the experimental inhibition efficiency. High E_{binding} value means strong interaction intensity between the inhibitor molecule and iron surface, which commonly leads to high inhibition efficiency. Therefore, from the aspect of MD simulation, the values of E_{binding} are expected as the critical factors to predict the inhibitive performance.

Table 5. Interaction and binding energies between penicillin derivatives and Fe (110) surface in aqueous solution.

Inhibitor	$E_{\text{Fe-inhibitor}}$	E_{binding}
Penicillin G	-136.5	136.5
Oxacillin	-186.2	186.2
Penicillin V	-163.7	163.7
Amoxicillin	-184.8	184.8

4. CONCLUSIONS

In this study, measurements including weight loss and Tafel polarization were adopted to investigate inhibitive properties of the four penicillin derivatives as corrosion inhibitors on mild steel. The inhibition mechanisms were further studied by quantum chemistry and MD simulations. From the obtained results, the following conclusions are summarized:

(1) The four penicillin derivatives are all excellent mix-type inhibitors for the corrosion of mild steel in 1.0 M HCl and the inhibition efficiencies increase with increasing the concentration of the inhibitors. Inhibition efficiency follows the order: oxacillin>amoxicillin>penicillin V>penicillin G.

(2) There are the good correlations observed between quantum chemical parameters and experimentally obtained results. The inhibitive performance can be explained on the basis of global and local reactivity of the inhibitors.

(3) The MD simulations suggest that the penicillin derivatives spontaneously adsorb onto metal surface by the active adsorption centres within the molecules and provide the most stable adsorption configurations. The order of E_{binding} coincides with the experimental inhibition efficiency. With the help of theoretical calculations, the screening tests for corrosion inhibitors will be clear directional and efficient.

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