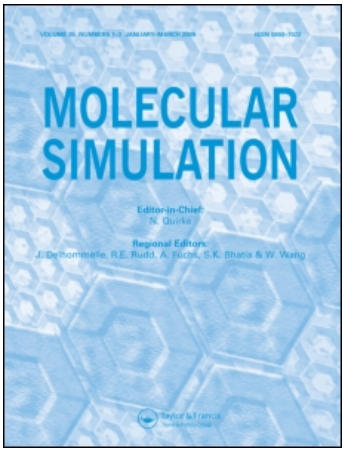

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Part 3. Theoretical study on some amino acids and their potential activity as corrosion inhibitors for mild steel in HCl

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Part 3. Theoretical study on some amino acids and their potential activity as corrosion inhibitors for mild steel in HCl

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Quantum chemical parameters, namely energy of the highest occupied molecular orbital, energy of the lowest unoccupied molecular orbital, energy gap, dipole moment, total energy, total electronic energy, core–core repulsion, ionisation potential, cosmo area, cosmo volume and other quantum descriptors [calculated from PM6, PM3, AM1, RM1 and modified neglect of diatomic overlap (MNDO) Hamiltonians], have been used to predict the corrosion inhibition potential of asparagine, aspartic acid, glutamine and glutamic acid. The results obtained indicate that the trend for the variation of the inhibition efficiencies of the compound is in the order: glutamine > asparagine > aspartic acid > glutamic acid. There is a strong agreement between some quantum chemical parameters and the experimental inhibition efficiencies. In order to establish the sites for electrophilic and nucleophilic attacks, condensed Fukui function, condensed softness and relative nucleophilicity/electrophilicity were considered. The results reveal that the sites for nucleophilic attacks in aspartic acid and glutamine are at the nitrogen atom (N5) but at the carbon atom (C3) for asparagine and glutamic acid. The sites for electrophilic attacks are at the oxygen atom (O9, for aspartic acid), carbon atom (C6, for asparagine), oxygen atom (O10, for glutamic acid) and nitrogen atom (N9, for glutamine).

Keywords: corrosion; inhibitors; amino acids; quantum chemical study; density functional theory

Abbreviations: χ, electronegativity; η, global hardness; ΔE, energy gap; μ, dipole moment; σ, chemical potential; C–C, core–core repulsion energy; CosAr, cosmo area; CosVol, cosmo volume; DFT, density functional theory; EA, electron affinity; EE, electronic energy of a molecule; E_{HOMO}, energy of the highest occupied molecular orbital; E_{LUMO}, energy of the lowest unoccupied molecular orbital; $E_{(N-1)}$, ground-state energy of the system with $N-1$ electrons; $E_{(N)}$, ground-state energy of the system with N electrons; $E_{(N+1)}$, ground-state energy of the system with $N+1$ electrons; f^+, Fukui function for the nucleophile; f^-, Fukui function for the electrophile; S^+, global softness for the nucleophile; S^-, global softness for the electrophile; IP, ionisation potential; q, Mulliken charge; Q_{ads}, heat of adsorption; QSAR, quantitative structure–activity relation; R, gas constant; S, global softness; TE, total energy of the molecule; AM1, Austin model 1; PM3, parametric method number 3; PM6, parametric method number 6; RM1, Recife model; MNDO, modified neglect of diatomic overlap

1. Introduction

Most corrosion inhibitors are organic compounds containing hetero-atoms in their aromatic or cyclic structures [1–4]. For these compounds, the presence of the hetero-atoms (such as N, S, P, O) and multiple bonds, in addition to some functional groups, facilitates the adsorption of the inhibitor on the surface of the metal [5,6]. It has also been found that the inhibitory potentials of such compounds are dependent on molecular size, molecular mass, internal structure, the nature and adsorptive tendencies of the hetero-atoms [7]. Other factors include the characteristics of the environment in which it acts, the nature of the metal surface, electrochemical potential at the interface, the structure of the inhibitor itself, which includes the number of adsorption-active centres in the molecule, their charge density, the molecule size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metal surface [8].

Some quantum mechanical studies have successfully linked the corrosion inhibition efficiency with molecular properties for different kinds of organic compounds [9]. Despite the large number of organic compounds, the choice of an appropriate corrosion inhibitor for a particular system is restricted by the specificity of the inhibitors and by the great variety of corrosion systems. In spite of the overwhelming success recorded on the use of heterocyclic compounds as corrosion inhibitors in several metallic systems using aqueous acids, the major disadvantage of most inhibitors is their toxicity and non-biodegradable nature [10]. According to Olivares-Xometl et al. [11], trends in environmental protection and ecological policies for the use of chemicals have changed the traditional approach of corrosion inhibition science. Currently, research is focused

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on producing and testing environmentally friendly corrosion inhibitors. A feasible solution to this problem is the use of corrosion inhibitors derived from plant extracts, amino acids and drugs [12–15]. Amino acids constitute an important potential class of corrosion inhibitors and have been successfully used in many practical applications, because they are friendly to the environment and have very low toxicity [16].

The objective of the present study is to present theoretical models of the electronic and molecular structures of asparagine, aspartic acid, glutamine and glutamic acid. The chemical and optimised structures of the compounds are presented in Figure 1. Substituent constants, quantum chemical descriptors and local selectivity indices shall be used to predict the inhibition potentials of these amino acids.

2. Computational technique

Quantum chemical calculations were carried out using PM6, PM3, AM1, RM1 and MNDO Hamiltonians in the MOPAC 2008 program [17]. Calculations were performed on an HP-compatible Pentium V (2.0 GHz and 4 GB RAM) computer. The following quantum chemical indices were calculated: the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the dipole moment (μ), the total energy (TE), the cosmo area (CosAr), the cosmo volume (CosVol) and the ionisation potential (IP). *Ab initio* parameters were computed by selecting the MP2 and B3LYP correlation types in the GAMES program while the basis set for the calculation was 6-31G [18]. The following *ab initio* parameters were calculated: total charge of the molecules, electron density and Mulliken charges on the atom.

3. Substituent constants

Table 1 presents the values of some substituent constants calculated for asparagine, aspartic acid, glutamic acid and glutamine. The average experimental inhibition efficiencies of the studied amino acids are also presented in Table 1. The inhibition efficiencies are average values obtained from gasometric, gravimetric and thermometric methods. Substituent constants are empirical quantities which account for the variation of the structure and do not depend on the parent structure but vary with the substituent [19,20].

The total molar polar surface area (tPSA) of a molecule is a useful parameter for predicting molecular transport properties. Polar surface area is defined as a sum of surfaces of polar atoms (usually oxygen, nitrogen and attached hydrogen) in a molecule. This parameter has been found to correlate strongly with the extent of absorption, and monolayer permeability in some biochemical reactions [21]. From the results obtained for the studied amino acids, it can be stated that, based on the tPSA, the inhibition efficiencies of glutamine and glutamic acid are expected to be closely related but should be better than those of asparagine and aspartic acid. On the other hand, the molar refractivity (MR) and the calculated molar

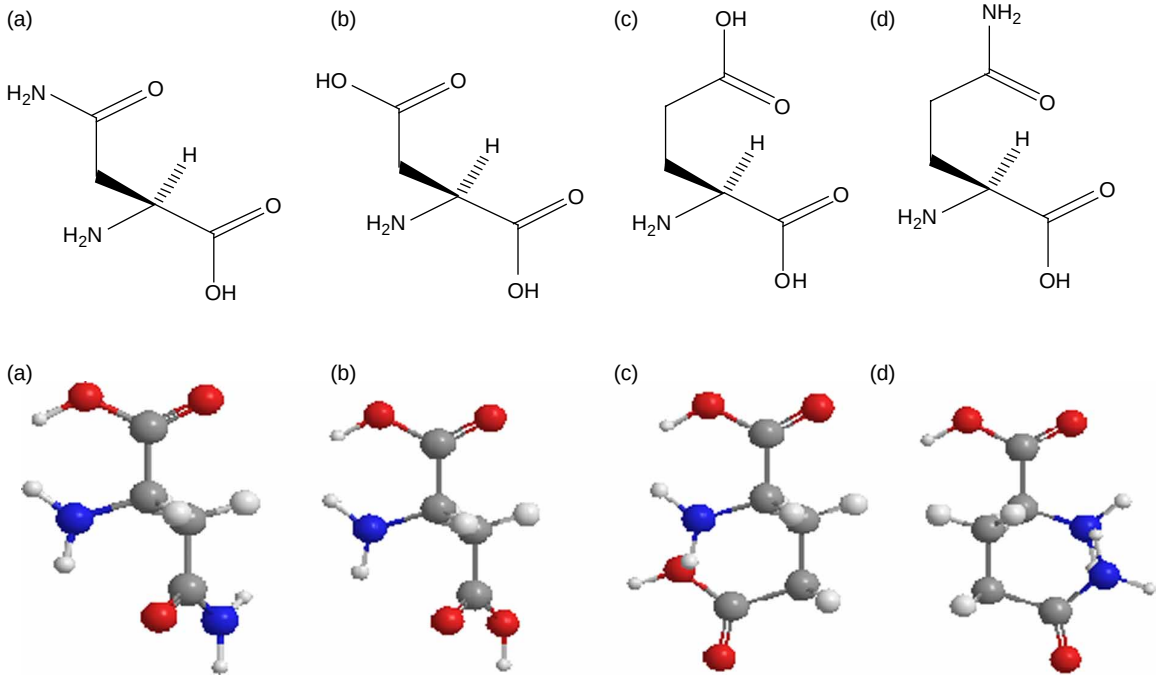

Figure 1. Chemical and optimised structures of (a) asparagine, (b) aspartic acid, (c) glutamic acid and (d) glutamine.

Table 1. Substituent constants for asparagine, aspartic acid, glutamic acid and glutamine.

Properties	Asparagine	Aspartic acid	Glutamic acid	Glutamine
Log *P*	− 2.33	− 1.67	− 1.39	− 2.05
C log *P*	− 1.84	− 0.96	− 0.84	− 1.52
tPSA	106.41	100.62	100.62	106.41
MR (cm^3/mol)	28.13	25.74	30.33	32.73
CMR	2.99	2.78	3.24	3.46
Inhibition efficiency (%)	71.76	64.83	63.14	84.54

refractivity (CMR) of a compound measure the size and polarisability of a substituent. MR is derived from the Lorentz–Lorenz equation. It is a function of the refractive index (n), the molecular weight (MW) and the density of the liquid (d), and can be expressed as follows:

$$\mathrm{MR} = \frac{n^2 - 1}{n^2 + 1} \times \frac{\mathrm{MW}}{d}. \quad (1)$$

Based on the calculated values of MR and CMR, the inhibition efficiencies of the four amino acids follow the trend, glutamine > glutamic acid > asparagine > aspartic acid. The predicted trend can also be analysed as follows. From Equation (1), MR is directly proportional to the MW of the compound and, as a rule, the inhibition efficiency of an organic compound, having a similar parent structure, is expected to increase with increase in MW. However, the results obtained from experiments reveal that the trend for the variation of the inhibition efficiency of the studied amino acids is glutamine > asparagine > aspartic acid > glutamic acid. Therefore, data obtained for CMR and MR alone cannot be used to adequately predict the inhibition efficiency of these compounds.

Log *P* and *C* log *P* are substituent constants that account for the hydrophobicity of an actual molecule. Hydrophobicity of organic molecules increases with decreasing water solubility. In corrosion studies, hydrophobicity is related to the mechanism of formation of the oxide/hydroxide layer on the metal surface (which reduces the corrosion process drastically). From the results obtained, based on the decreasing value of log *P* and *C* log *P*, the inhibition efficiencies of the studied amino acids follow the trend, asparagine > glutamine > aspartic acid > glutamic acid. This trend conflicts with the one obtained from other substituent constants, indicating that log *P* and *C* log *P* may not be unique parameters for the prediction of corrosion inhibition mechanism.

The major difference between asparagine/aspartic acid and glutamine/glutamic acid is the presence of the amino group in asparagine/glutamine and the hydroxyl group in aspartic acid/glutamic acid. Both amino and hydroxyl groups are electron-releasing groups, hence they can release the electron into the reaction centre of the molecules, leading to the stabilisation of electron-deficient carbocations and, consequently, better inhibition of metallic corrosion. However, the electron-releasing effect of —NH_2 appears to be relatively stronger than that of —OH, hence the differences in inhibition potentials. Empirical consideration of the importance of substituent constants as descriptors for corrosion inhibition mechanism should be done with reservation and on the assumption that the parent molecule is not attacked during the inhibition process.

4. Global reactivity

The values of energy of the frontier molecular orbital (namely E_{HOMO}, E_{LUMO} and LUMO–HOMO energy gap) are important quantum chemical descriptors for molecular reactivity [22]. According to the frontier molecular theory, the formation of a transition state is due to an interaction between frontier molecular orbitals (HOMO and LUMO) of reacting species [23]. These descriptors have also been used in corrosion studies. E_{HOMO} is associated with electron-donating ability of the inhibitor. Therefore, the inhibition efficiencies of inhibitors are expected to increase with increasing value of E_{HOMO} since this indicates increasing ease of donating electrons to the vacant d-orbital of the metal (such as Fe). On the other hand, E_{LUMO} is associated with the ability of the molecule to accept electron, therefore decreasing values of E_{LUMO} suggest better inhibition efficiencies [24]. The energy gap of an inhibitor ($\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$) is an important stability index and is used to develop theoretical models for explaining structure and conformation barriers in molecular systems. The smaller the energy gap, the better is the expected inhibition efficiency of the compound [25]. Table 2 shows the quantum chemical parameters (calculated from PM6, PM3, AM1, RM1 and MNDO Hamiltonians) for glutamine, glutamic acid, asparagine and aspartic acid. As can be seen from Table 2, based on the increasing value of E_{HOMO} and decreasing value of E_{LUMO} as well as the decreasing value of $E_{\mathrm{LUMO-HOMO}}$, the inhibition efficiency of the studied amino acids is expected to increase in the following order: glutamine > asparagine > aspartic acid > glutamic acid. This trend is consistent with the experimental results presented in Table 1.

The IP of a molecule defines the ability of the molecule to lose electrons. This suggests that IP is closely related to E_{HOMO}; hence, from the calculated values of IP, the

Table 2. Calculated quantum chemical parameters for the amino acids studied.

Models	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{LUMO-HOMO}$ (eV)	TE (eV)	EE (eV)	C–C (eV)	CosAr (Å^2)	CosVol (Å^3)	IP (eV)	μ (Debye)
Aspartic acid										
PM6	−9.34	0.09	9.43	−1930.70	−8039.21	6180.49	151.37	145.12	9.34	3.16
PM3	−8.92	0.74	9.66	−1918.99	−8141.95	6222.97	151.37	145.12	8.92	2.98
AM1	−9.53	0.90	10.43	−2097.72	−8361.45	6263.73	151.37	145.12	9.53	2.90
RM1	−9.53	0.87	10.40	−2076.46	−8344.59	6268.13	151.37	145.12	9.53	2.95
MNDO	−9.92	0.69	10.62	−2106.35	−8380.75	6274.40	151.37	145.12	9.92	3.02
Asparagine										
PM6	−9.68	0.03	9.71	−1832.05	−8067.24	6235.22	152.61	147.24	9.68	3.70
PM3	−9.30	0.73	10.03	−1802.29	−8033.08	6230.79	152.61	147.24	9.30	3.34
AM1	−9.87	0.89	10.76	−1997.20	−8283.21	6286.00	152.61	147.24	9.87	3.22
RM1	−9.88	0.84	10.72	−1983.76	−8282.72	6298.96	152.61	147.24	9.88	3.27
MNDO	−10.28	0.77	11.04	−2004.48	−8301.91	6296.91	152.61	147.24	10.28	3.14
Glutamic acid										
PM6	−8.61	0.27	8.88	−2077.24	−9779.60	7702.35	162.09	161.41	8.61	3.18
PM3	−8.54	0.74	9.28	−2064.88	−9799.70	7734.81	162.09	161.41	8.54	2.83
AM1	−8.70	0.90	9.61	−2248.86	−10033.62	7784.76	162.09	161.41	8.70	2.88
RM1	−8.61	0.88	9.50	−2226.67	−10023.36	7796.69	162.09	161.41	8.61	2.94
MNDO	−8.78	0.56	9.34	−2257.39	−10054.57	7797.18	162.09	161.41	8.78	2.85
Glutamine										
PM6	−9.62	0.44	10.06	−1982.18	−9235.39	7253.21	175.49	169.39	9.62	7.85
PM3	−9.39	1.10	10.49	−1952.14	−9183.53	7231.39	175.49	169.39	9.39	6.97
AM1	−9.92	1.22	11.14	−2153.39	−9442.32	7288.93	175.49	169.39	9.92	6.91
RM1	−9.90	1.19	11.09	−2138.03	−9449.78	7311.75	175.49	169.39	9.90	7.00
MNDO	−10.35	1.08	11.44	−2161.37	−9462.75	7301.38	175.49	169.39	10.35	6.74

strength of the inhibition efficiencies of the studied amino acid is similar to that obtained from E_{HOMO} data and is also consistent with the experimental results. The dipole moment of a compound (μ) refers to the quality of a system to behave like a dipole. The dipole moment is the measured polarity of a polar covalent bond. It is defined as the product of the magnitude of charge on the atoms and the distance between the two bonded atoms. On the trend of the variation of μ with inhibition efficiency, the literature reveals that there are some irregularities in the relationship between dipole moment and inhibition efficiency. However, the present results indicate that the dipole moment decreases in the trend similar to that obtained for E_{LUMO}, E_{HOMO}, $E_{LUMO-HOMO}$ and IP, and with the experimental results.

El Ashry et al. [25] noted that core–core repulsion (C–C) energy is a quantum chemical parameter that may have excellent correlation with inhibition efficiency. They reported that the inhibition efficiency of some Schiff base decreases with increasing value of C–C energy. On the other hand, the inhibition efficiencies were found to increase with increasing values of CosAr and CosVol. This study on quantum chemical descriptors has been extended to include the total and the electronic energies of the molecules. From the results, it is evident that, based on the increasing values of the TE and electronic energy (EE) as well as the decreasing value of C–C energy, the expected trend for the variation of the inhibition potentials of the studied amino acid is glutamic acid > glutamine > aspartic acid > asparagine, whereas based on the decreasing value of CosAr and CosVol, the following order was obtained: glutamine > glutamic acid > asparagine > aspartic acid. Both results conflict with those obtained from experiments, indicating that there may be some irregularities in using these parameters (namely TE, EE, CosVol and CosAr) as predictors for the inhibition of the corrosion of mild steel in HCl by the studied amino acids. On the other hand, strong correlations were found between experimental inhibition efficiencies and the other quantum chemical parameters (namely E_{HOMO}, E_{LUMO}, $E_{LUMO-HOMO}$, IP and μ). Table 3 presents the correlation coefficients between the experimental inhibition efficiencies and some quantum chemical parameters (namely E_{HOMO}, E_{LUMO}, $E_{LUMO-HOMO}$, IP and μ). Table 3 reveals that, although there was no significant difference between the correlation coefficients obtained from the respective Hamiltonians, values of r obtained from the PM6 and PM3 calculations were relatively better than those obtained from other Hamiltonians.

Table 4 shows values of some quantum chemical descriptors calculated for glutamic acid, glutamine, asparagine and aspartic acid. From the calculated values of the TE of the cation (E_{N-1}), the anion (E_{N+1}) and that of the neutral molecules (E_N), the values of ionisation

Table 3. Correlation coefficient (r) between experimental inhibition efficiencies and some quantum chemical parameters.

	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{LUMO-HOMO}$ (eV)	IP (eV)	μ (eV)
PM6	0.846	−0.913	0.958	0.846	0.959
PM3	0.846	−0.914	0.958	0.846	0.960
AM1	0.734	−0.912	0.857	0.734	0.951
RM1	0.710	−0.880	0.839	0.710	0.950
MNDO	0.711	−0.711	0.983	0.809	0.944

energy (IE) and electron affinity (EA) were obtained using the following equations:

$$\mathrm{IE} = E_{N-1} - E_N, \tag{2}$$

$$\mathrm{EA} = E_N - E_{N+1}. \tag{3}$$

The report shows that the values of IE calculated from Equation (2) correlated strongly with those obtained from E_{HOMO} ($r = 0.9789$). Therefore, the results obtained from either method are excellent in predicting the inhibitive behaviour of the inhibitors. The negative values obtained for EA indicate that the conjugated complexes of the amino acids are electrophilic [26].

The dependence of the calculated values of E_{HOMO} and E_{LUMO} on the IEs and EAs was investigated through correlation analysis. The R^2 values for the correlation between E_{HOMO} and IE for aspartic acid, asparagine, glutamic acid and glutamine were 0.9064, 0.8897, 0.6068 and 0.9177, respectively. However, for the correlation between E_{LUMO} and EA, the corresponding R^2 values were 0.60332, 0.6770, 0.9340 and 0.7177, respectively. From these correlations, it can be stated that glutamine and asparagine have a higher potential towards the binding of electron-donating ligands than glutamic acid and aspartic acid. This finding supports the proposed order for the expected and actual variation of the inhibition efficiencies of these compounds (i.e. glutamine > asparagine > glutamic acid > aspartic acid).

Using DFT study, the ground-state energy $E(\rho)$ of an atom or a molecule is expressed in terms of its electron density $\rho(r)$. Under a constant external potential, $v(r)$, two chemical reactivity indices, a chemical potential (σ) and global hardness (η), are defined as the first and second derivatives of $E(\rho)$ with respect to the number of electrons $N(\mu) = (\delta E/\delta N)_{V(r)}$ and $\eta = (\delta^2 E/\delta N^2)_{V(r)}$, respectively. Using the finite-difference approximation, the global softness (S) was evaluated using the following equation [27]:

$$S = \frac{1}{[(E_{(N+1)} - E_N) - (E_N - E_{(N-1)})]}. \tag{4}$$

The global hardness is the inverse of the global softness ($\eta = 1/S$). Values of S and η calculated from Equation (4) are presented in Table 4. The hard and soft

Table 4. Quantum chemical descriptors for the amino acids studied.

Model	E_N	E_{N-1}	E_{N+1}	IE (eV)	EA (eV)	χ	S (eV^{-1})	η (eV)	δ
Aspartic acid									
PM6	−1930.70	−1922.10	−1931.12	8.61	−0.42	4.51	0.12	8.19	0.15
PM3	−1918.99	−1910.73	−1918.76	8.26	−0.23	4.02	0.12	8.49	0.18
AM1	−2097.72	−2089.03	−2097.27	8.68	−0.45	4.12	0.11	9.13	0.16
RM1	−2076.46	−2067.90	−2076.09	8.56	−0.38	4.09	0.11	8.94	0.16
MNDO	−2106.35	−2097.24	−2106.11	9.11	−0.24	4.44	0.11	9.35	0.14
Asparagine									
PM6	−1832.05	−1823.08	−1832.50	8.96	0.46	4.71	0.12	8.51	0.13
PM3	−1802.29	−1793.68	−1801.64	8.61	−0.65	3.98	0.11	9.26	0.16
AM1	−1997.20	−1988.20	−1996.83	9.00	−0.37	4.32	0.11	9.37	0.14
RM1	−1983.76	−1974.87	−1982.67	8.89	−1.09	3.90	0.10	9.98	0.16
MNDO	−2004.48	−1995.03	−2004.21	9.45	−0.27	4.59	0.10	9.72	0.12
Glutamic acid									
PM6	−2077.24	−2069.51	−2077.53	7.73	0.29	4.01	0.13	7.44	0.20
PM3	−2064.88	−2057.15	−2064.37	7.74	−0.51	3.61	0.12	8.25	0.21
AM1	−2248.86	−2241.17	−2248.27	7.69	−0.59	3.55	0.12	8.28	0.21
RM1	−2226.67	−2219.16	−2226.13	7.51	−0.54	3.49	0.12	8.05	0.22
MNDO	−2257.39	−2249.59	−2257.42	7.80	0.03	3.91	0.13	7.77	0.20
Glutamine									
PM6	−1982.18	−1973.26	−1982.25	8.92	0.07	4.50	0.23	4.43	0.28
PM3	−1952.14	−1943.39	−1951.23	8.75	−0.91	3.92	0.21	4.83	0.32
AM1	−2153.39	−2144.29	−2152.70	9.10	−0.70	4.20	0.20	4.90	0.29
RM1	−2138.03	−2129.06	−2136.67	8.97	−1.36	3.81	0.19	5.16	0.31
MNDO	−2161.37	−2151.80	−2160.78	9.57	−0.59	4.49	0.20	5.08	0.25

Table 5. Global and local selectivity parameters for N, O and C atoms in the amino acids studied (calculated from DFT-B3YLP-631G**).

Atom no.	f^+ (|e|)	f^- (|e|)	S^+ (eV |e|)	S^- (eV |e|)	S^+/S^-	S^-/S^+
Aspartic acid						
1C	−0.519	−0.044	−0.889	−0.075	11.841	−0.006
2O	0.378	−0.048	0.648	−0.083	−7.852	0.011
3C	0.025	0.110	0.042	0.189	0.223	0.847
4O	0.550	−0.053	0.943	−0.091	−10.402	0.009
5N	0.763	−0.326	1.307	−0.558	−2.342	0.238
6C	0.289	0.034	0.495	0.058	8.583	0.007
7C	−0.500	−0.024	−0.857	−0.041	21.093	−0.002
8O	0.394	−0.100	0.675	−0.172	−3.931	0.044
9O	0.574	0.016	0.984	0.028	35.448	0.001
Asparagine						
1C	−0.125	−0.039	−0.218	−0.068	3.229	0.310
2O	−0.141	−0.062	−0.245	−0.107	2.282	0.438
3C	0.050	0.079	0.087	0.138	0.631	1.585
4O	−0.051	−0.049	−0.089	−0.086	1.038	0.963
5N	−0.006	−0.206	−0.010	−0.358	0.028	35.877
6C	0.045	0.018	0.078	0.031	2.473	0.404
7C	−0.074	−0.040	−0.129	−0.069	1.866	0.536
8O	−0.113	−0.166	−0.197	−0.288	0.684	1.462
9N	−0.013	−0.021	−0.022	−0.036	0.603	1.660
Glutamic acid						
1C	−13.932	−0.036	−26.753	−0.069	386.286	0.003
2O	−9.409	−0.037	−18.066	−0.071	254.146	0.004
3C	−3.533	0.077	−6.783	0.147	−46.129	−0.022
4O	−9.441	−0.045	−18.129	−0.087	208.904	0.005
5N	3.597	−0.239	6.907	−0.460	−15.028	−0.067
6C	2.646	0.044	5.081	0.084	60.260	0.017
7C	5.075	0.011	9.745	0.020	483.830	0.002
8C	5.552	−0.014	10.661	−0.026	−412.189	−0.002
9O	6.388	−0.108	12.266	−0.208	−59.013	−0.017
10O	6.520	0.040	12.519	0.076	164.327	0.006
Glutamine						
1C	−0.059	−5.475	−0.095	−8.888	0.011	93.591
2O	−0.100	−6.392	−0.162	−10.376	0.016	64.256
3C	0.021	−5.889	0.034	−9.559	−0.004	−281.265
4O	−0.015	−6.549	−0.024	−10.630	0.002	437.355
5N	0.046	−5.781	0.074	−9.384	−0.008	−127.118
6C	0.024	−4.039	0.039	−6.556	−0.006	−167.140
7C	0.040	5.898	0.064	9.574	0.007	148.693
8C	−0.065	13.210	−0.105	21.443	−0.005	−203.817
9N	−0.025	11.233	−0.041	18.233	−0.002	−443.545
10O	−0.083	8.000	−0.134	12.985	−0.010	−96.767

acids and bases (HSAB) principle requires that a reaction between an acid and a base is favoured when global softness difference is minimal. Also, a hard molecule has a large energy gap while a soft molecule has a low energy gap, hence based on the calculated value of global softness and global hardness, the inhibition efficiencies of the studied amino acids follow the order similar to the one obtained from experiment. However, the use of data obtained from only global softness and hardness data may not confer overall confidence in predicting the inhibitory potentials of organic compounds such as amino acids. This implies that other quantum chemical parameters must be taken into consideration.

The fraction of electron transferred, δ, was calculated using Equation (5) [28],

$$\delta = \frac{\chi_{\mathrm{Fe}} - \chi_{\mathrm{inh}}}{2(\eta_{\mathrm{Fe}} + \eta_{\mathrm{inh}})}, \tag{5}$$

where χ_{Fe} and χ_{inh} are the electronegativity of Fe and the inhibitor, respectively. $\chi = (\mathrm{IP}+\mathrm{EA})/2$. η_{Fe} and η_{inh} are the global hardness of Fe and the inhibitor, respectively. In order to validate Equation (5) for our study, the theoretical values of $\chi_{\mathrm{Fe}} = 7$ eV and $\eta_{\mathrm{Fe}} = 0$ were used for the computation of δ values for the various models. Calculated values of δ for the studied amino acids are also presented in Table 4.

Table 6. Global and local selectivity parameters for N, O and C atoms in the amino acids studied (calculated from MP2-631G**).

Atom no.	f^+ (|e|)	f^- (|e|)	S^+ (eV |e|)	S^- (eV |e|)	S^+/S^-	S^-/S^+
Aspartic acid						
1C	−0.519	−0.044	−0.889	−0.075	11.841	−0.006
2O	0.378	−0.048	0.648	−0.083	−7.852	0.011
3C	0.025	0.110	0.042	0.189	0.223	0.847
4O	0.550	−0.053	0.943	−0.091	−10.402	0.009
5N	0.763	−0.326	1.307	−0.558	−2.342	0.238
6C	0.289	0.034	0.495	0.058	8.583	0.007
7C	−0.500	−0.024	−0.857	−0.041	21.093	−0.002
8O	0.394	−0.100	0.675	−0.172	−3.931	0.044
9O	0.574	0.016	0.984	0.028	35.448	0.001
Asparagine						
1C	−0.284	−0.002	−0.494	−0.003	147.841	0.007
2O	−0.243	−0.055	−0.422	−0.096	4.398	0.227
3C	0.079	0.019	0.137	0.033	4.107	0.244
4O	−0.066	−0.032	−0.114	−0.055	2.075	0.482
5N	−0.011	−0.011	−0.019	−0.020	0.938	1.066
6C	0.028	0.015	0.049	0.026	1.901	0.526
7C	−0.017	−0.019	−0.030	−0.032	0.939	1.065
8O	−0.061	−0.452	−0.107	−0.786	0.136	7.380
9N	−0.003	−0.081	−0.005	−0.142	0.037	27.282
Glutamic acid						
1C	−0.281	−0.032	−0.092	−0.011	8.774	0.114
2O	−0.241	−0.035	−0.079	−0.012	6.825	0.147
3C	0.077	0.122	0.025	0.040	0.633	1.579
4O	−0.063	−0.046	−0.021	−0.015	1.359	0.736
5N	−0.004	−0.390	−0.001	−0.128	0.011	90.850
6C	0.037	0.042	0.012	0.014	0.885	1.130
7C	−0.002	0.003	−0.001	0.001	−0.718	−1.393
8C	0.008	0.028	0.003	0.009	0.268	3.728
9O	−0.057	−0.104	−0.019	−0.034	0.546	1.833
10O	0.035	0.092	0.012	0.030	0.381	2.625
Glutamine						
1C	−0.272	−0.017	−0.441	−0.027	16.402	0.061
2O	−0.254	−0.095	−0.412	−0.155	2.666	0.375
3C	0.068	0.187	0.110	0.303	0.362	2.764
4O	−0.059	−0.055	−0.095	−0.089	1.071	0.934
5N	−0.006	−0.473	−0.009	−0.768	0.012	86.153
6C	0.041	0.051	0.066	0.083	0.797	1.254
7C	0.001	0.017	0.002	0.027	0.061	16.465
8C	−0.010	−0.011	−0.016	−0.018	0.915	1.093
9N	−0.009	−0.015	−0.014	−0.025	0.577	1.734
10O	−0.012	−0.028	−0.020	−0.045	0.435	2.302

The results indicate that δ values obtained for glutamine are the largest, which implies that glutamine is the best inhibitor as revealed by experimental results.

5. Local selectivity

In discussing the local selectivity of a corrosion inhibition process, it is significant to state that not only the π-electrons of the amino acids can enter the unoccupied orbital of a metal (such as Fe) but the π*-orbital can also accept electrons from the d-orbital of the metal to form a feedback bond [28]. This concept enables us to consider the reactivity criteria of local type such as the Fukui function. The derivative of the electronic density for an N-electron system, $\rho(r)$, with respect to the total number of electrons will have one value when evaluated from the right and a different value when evaluated from the left. These values are defined as follows:

$$f^+(r) = \left(\frac{\delta\rho(r)}{\delta N}\right)^+ = \rho_{N+1}(r) - \rho_N(r), \tag{6}$$

$$f^-(r) = \left(\frac{\delta\rho(r)}{\delta N}\right)^- = \rho_N(r) - \rho_{N-1}(r). \tag{7}$$

Equation (6) is applicable to a situation where N increases from N to $N+1$ (i.e. anion), while Equation (7) describes a case when N decreases from N to $N-1$ (i.e. cation). The implication of Equations (6) and (7) is that the molecular sites with larger values of f^+ are the sites for the

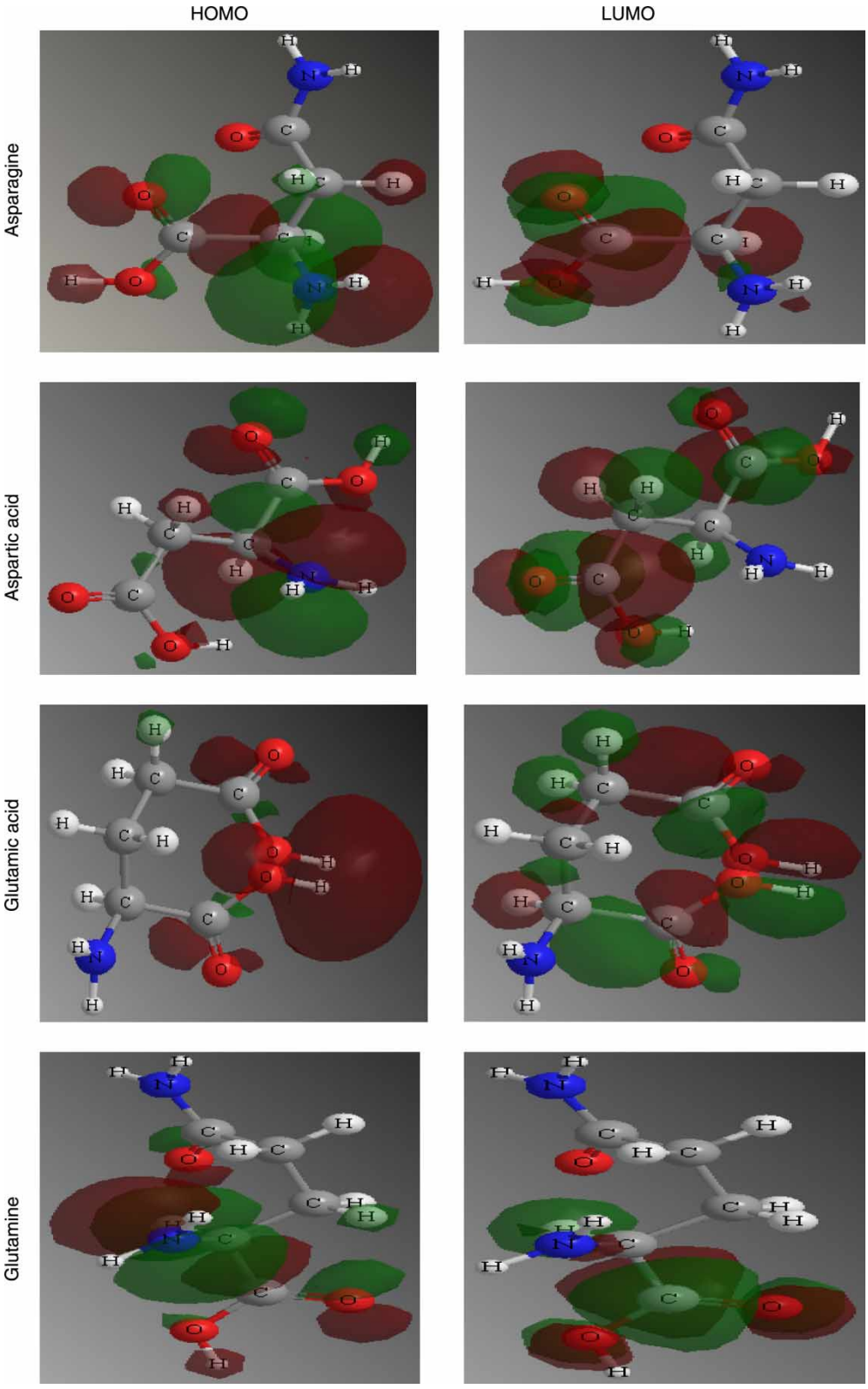

Figure 2. Molecular orbital of studied amino acids showing the HOMO and LUMO.

nucleophilic attack while the sites with larger value of f^- are the sites for the electrophilic attack (i.e. the preferred site through which the molecule will donate charge when attacked by an electrophilic agent). However, a more useful approach to the molecular Fukui function is provided by the condensed Fukui function. In the finite-difference approximation, the condensed Fukui functions of an atom x in a molecule that contained N electron are defined in Equations (8) and (9),

$$f_{x+} = q_{(N+1)} - q_{(N)}, \tag{8}$$

$$f_{x-} = q_{(N)} - q_{(N-1)}. \tag{9}$$

From molecular orbital theory, an additional electron will occupy the LUMO whereas upon ionisation, an electron will leave the HOMO, hence the condensed Fukui functions (f_{x+} and f_{x-}) are related to the LUMO and HOMO, respectively. The local softness s_x for an atom x is the product of condensed Fukui function and the global softness (S) as shown in Equations (10) and (11),

$$S_{x+} = S(f_{x+}), \tag{10}$$

$$S_{x-} = S(f_{x-}). \tag{11}$$

The local softness contains information similar to the Fukui function in addition to information about the total molecular softness, which is related to the global reactivity with respect to a reaction partner. Finally, the relative nucleophilicity (s_{x-}/s_{x+}) and the relative electrophilicity (s_{x-}/s_{x+}) are other indices that can be used to predict the reactivity sequences of a compound towards nucleophilic and electrophilic attacks. Tables 5 and 6 present the values of f_{x+}, f_{x-}, S_{x+}, S_{x-}, S_{x-}/S_{x+} and S_{x-}/S_{x+} calculated using DFT-B3YLP-631G and MP2-631G (in the GAMES program). Values of Mulliken charge for the cation, anion and neutral molecules were used for the respective calculation. These values are also presented in the tables. From the results presented in Tables 5 and 6, it is most likely that the sites for nucleophilic attacks in aspartic atom acid and glutamine are at the nitrogen atom (N5) but at the carbon atom (C3) for asparagine and glutamic acid. The sites for electrophilic attacks are at the oxygen atom (O9, for aspartic acid), the carbon atom (C6, for asparagine), the oxygen atom (O10 for glutamic acid) and the nitrogen atom (N9 for glutamine). This information is also presented in Figure 2. Figure 2 shows the HOMO and LUMO molecular surfaces of the studied amino acids (calculated from Huckel theory). From the figure, it is evident that the sites for electrophilic and nucleophilic attacks are consistent with the findings deduced from Fukui and global softness parameters.

6. Conclusion

The present study indicates that a combination of substituent constants, quantum chemical parameters and local selectivity indices can be used to predict the direction of the inhibition reactions and the sites for nucleophilic/electrophilic attacks with respect to asparagine, aspartic acid, glutamine and glutamic acid.

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