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INHIBITION OF STEEL CORROSION BY SOME SCHIFF AND MANNICH BASES: A THEORETICAL EVALUATION

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There is no doubt that the value and importance of using computational methods in corrosion science are becoming gradually recognized. Drilling deeper into the thought that certain molecular electronic descriptors such as ionization potential, electron affinity, HOMO–LUMO gap and dipole moment matter, because they present a unique solution to comprehend the inhibition properties of corrosion inhibitors, leads us to a further quandary. The reliability of such parameters is the subject of acrimonious debate, and thus, the present study is an extension of this attempt to contemplate earlier experimental results reported for some Schiff and Mannich bases as corrosion inhibitors for steel in neutral aqueous solutions by using density functional theory calculations. Due to the sources of uncertainties like the structure of the molecular model, the description of environmental efforts and errors related to the nature of quantum chemical methods, it was inferred that no coherent picture could be emerged about the corrosion inhibition properties of the studied compounds through calculated descriptors.

Keywords: carbon steel, corrosion, inhibitor, Schiff base, Mannich base, density functional theory.

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Introduction

Corrosion can be defined as an irreversible reaction of a material with its environment, which generally leads to deterioration in the material or its properties. Carbon steel is a basic structural metallic material for underground pipelines and constructions at temperatures below 230^{0}C owing to its resistance to alkaline (pH ~9–13) solutions. However, in environments that are close to neutral, with access to air, carbon steel is in an active state and corrodes with oxygen depolarization [1]. Limited resources and strong demand for the use of carbon steel in neutral solutions in electrochemical plants have motivated the development of several corrosion inhibitors which, when added in small concentrations, minimize or prevent corrosion [2]. Among employed corrosion inhibitors in the industrial area, organic inhibitors are the most used ones. These compounds protect metal against corrosion through chemical and/or physical adsorption processes, and are characterized by the presence of lone pair electrons of heteroatoms, functional groups and/or multiple bonds on their molecular skeletons, which act as the favorable sites of adsorption during the inhibitor-metal interactions [3].

Nitrogen-containing heterocyclic compounds as trenchant corrosion inhibitors of steel currently attract considerable interest [4–6]. What has also been emerging more powerfully in the past few years is the potential of the compounds either carrying imine or azomethine functional group (Schiff bases) or beta-amino ketones (Mannich bases) to inhibit the corrosion of ferrous materials [7,8]. In this context, Altsybeeva et al. [9] recently reported the successful use of some Schiff and Mannich bases (Fig. 1) as corrosion inhibitors of steel in neutral media. They carried out potentiodynamic polarization measurements to test the protective effect of those morpholine and benzotriazole derivatives for carbon steel corrosion in a mixture of NaCl and Na_2SO_4. Although their experimental work provides valuable information on the corrosion inhibition efficiencies of such compounds, a deep understanding of the inhibition properties remains unclear.

Experimental corrosion science has hugely

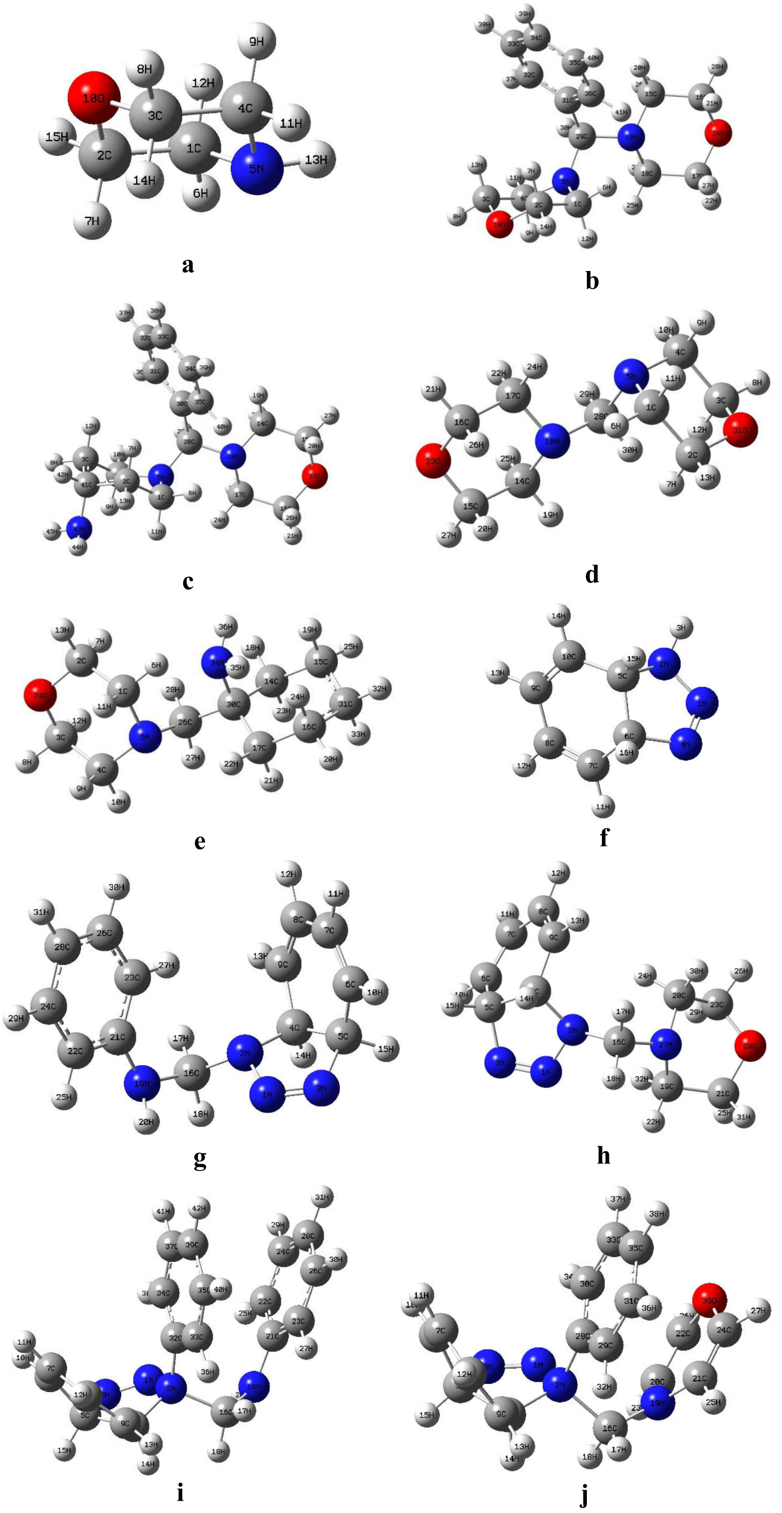

Fig. 1. Optimized structures at the M06-2X/DGDZVP level for (a) morpholine (M1), (b) dimorpholine phenylmethane (M2), (c) 1-(phenyl)-1-(morpholinomethyl)-cyclohexylamine (M3), (d) dimorpholinomethane (M4), (e) 1-morpholinomethylcyclohexylamine (M5), (f) benzotriazole (S1), (g) 1-cyclohexylaminomethylbenzotriazole (S2), (h) 1-morpholinomethylbenzotriazole (S3), (i) 1-(phenyl)-1-(cyclohexylaminomethyl)benzotriazole (S4), and (j) 1-(phenyl)-1-(morpholinomethyl) benzotriazole (S5) in aqueous phase

benefitted from the theoretical approaches for the past two decades, and the current easy access to quantum chemistry computer packages has immensely facilitated the work of the corrosion scientists, and the evergrowing application of quantum mechanical methods [10]. Prompted by the thriving application of theoretical calculations in corrosion inhibitor research, this paper attempts to elucidate the origin of the observed inhibition properties of ten compounds (morpholine, benzotriazole and their derivatives) (Fig. 1) by using density functional theory (DFT) method which has emerged as a powerful tool for analyzing different molecular properties.

Computational

Geometry optimization and frequency analysis of all the structures included in this study has been carried out using M06-2X/DGDZVP level of theory as implemented in Gaussian 09 program package [11]. The structures were reoptimized in the presence of water as implicit solvent; in this case, the continuum solvation model SMD was used. Global reactivity descriptors, namely, chemical potential (μ), chemical hardness (η) and electrophilicity index (ω), have been expressed using the following working formulae (Eqs. (1)–(4)) within the scope of conceptual density functional theory.

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\nu} \underset{r}{(\rightarrow)} \approx -\frac{(IP + EA)}{2} = \\ = \frac{E_{LUMO} + E_{HOMO}}{2} = \chi; \qquad (1)$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu} \underset{r}{(\rightarrow)} = \left(\frac{\partial \mu}{\partial N}\right)_{\nu} \underset{r}{(\rightarrow)} = \\ = \frac{E_{LUMO} - E_{HOMO}}{2}; \qquad (2)$$

$$S = (2\eta)^{-1}; \qquad (3)$$

$$\omega = \frac{\mu^2}{2\eta}, \qquad (4)$$

where μ is the Lagrange multiplier associated with the normalization constraint of DFT identified as the electronic chemical potential; E is the total energy; ν is the external potential; IP and EA are the vertical ionization potential and electron affinity of the system, respectively, they are given as $IP=-E_{HOMO}$ and $EA=-E_{LUMO}$, keeping the external potential fixed.

IP and EA have been calculated using Koopmans' theorem to avoid the time-consuming calculations. The fraction of electrons transferred (ΔN) is also calculated by the following equation:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} = \frac{\Phi - \chi_{inh}}{2\eta_{inh}}. \qquad (5)$$

In this equation, the work function Φ presents the theoretical value of electronegativity of iron ($\Phi=\chi_{Fe}=4.82$ eV), and the global hardness corresponds to the metallic bulk ($\eta_{Fe}=0$ eV) [12].

Results and discussion

As is known, the fusion of benzene and imidazole forms benzimidazole which is bicyclic in its nature (Fig. 1,f). An electronegative azole moiety with a benzene-like ring structure makes benzotriazole interesting to study with theoretical methods in surface science since it can primarily interact with metal surfaces through chemisorption. Furthermore, morpholine is a common chemical precursor in many organic syntheses due to the nucleophilic nitrogen lone pair. Taken together, the synthesis of Schiff and Mannich bases derived from either benzimidazole or morpholine scaffolds takes an important place in corrosion inhibitor research. Mannich bases are the end products of Mannich reaction which is a nucleophilic addition reaction that comprises the condensation of a compound with active hydrogen(s) with an amine (primary or secondary) and formaldehyde (any aldehyde) by using an acid or base catalyst. On the other hand, Schiff bases are the condensation products of primary amines with carbonyl compounds. Accruing evidence suggests that such compounds exist as neutral molecules in aqueous medium unless the acidity of the solution is changed [13]. The experimental data resorted to were predicated on the results of electrochemical tests in neutral solutions, and accordingly, neutral forms of these compounds were used for quantum chemical calculations. The fully optimized structures of the inhibitors at the M06-2X/DGDZVP level of theory are illustrated in Fig. 1. To adminiculate the DFT-optimized geometries of the compounds, some selected geometric parameters of morpholine, with reference atom numbering given in Fig. 1, are summarized in Table 1 and compared with those obtained experimentally for its crystal structure [14].

This comparison may serve as a convincing

Table 1

Selected geometric parameters for morpholine (see Fig. 1 for atom numbering scheme)

	This work	Experimental [14]
Bond lengths (Å)		
O_{10}–C_3	1.431	1.432 (2)
O_{10}–C_2	1.431	1.424 (3)
C_3–C_4	1.516	1.516 (3)
C_3–H_8	1.091	0.980
C_3–H_{14}	1.098	0.980
C_4–N_5	1.469	1.466 (3)
C_4–H_{11}	1.092	0.980
C_4–H_9	1.100	0.980
N_5–C_1	1.469	1.468 (2)
N_5–H_{13}	1.018	0.89 (3)
C_1–C_2	1.516	1.510 (3)
C_1–H_6	1.092	0.980
C_1–H_{12}	1.100	0.980
Bond angles (^{0})		
C_3–O_{10}–C_2	110.71	110.32 (16)
O_{10}–C_3–C_4	110.98	111.31 (18)
O_{10}–C_3–H_8	106.65	108.99
C_4–C_3–H_8	110.76	109.03
O_{10}–C_3–H_{14}	109.21	108.99
C_4–C_3–H_{14}	110.26	109.03
H_8–C_3–H_{14}	108.89	109.46
C_3–C_4–N_5	109.32	108.69 (17)
C_3–C_4–H_{11}	109.11	109.68
N_5–C_4–H_{11}	109.61	109.66
C_3–C_4–H_9	108.69	109.67
N_5–C_4–H_9	111.84	109.65
C_4–N_5–C_1	108.54	109.25 (15)

starting observation for the adaptness of the theoretical approach used here. A reasonably low difference between experimental and theoretical data was obtained. The C–N bond lengths are very uniform with a value of 1.469 Å, which is consistent with reference data and reveals that C–N is of the character of a single bond. The fit of the calculated bond angles is also consonant with the differences being less than 1^0. The predicted morpholine structure agrees rather closely with the experimentally determined conformation, given that the calculated results are for an isolated molecule.

Understood by analogy with affordances, it is a fairly deliberate way of calculating some other parameters such as the energies of the frontier molecular orbitals using the same predilection. The knowledge about the electronic structure of the inhibitors is crucial for a deeper understanding of their behavior in inhibition process. In particular, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is of large interest because it serves as an indicator for molecular properties like stability or reactivity [10]. The HOMO density is closely related to the charge transfer, whereas for an acceptor compound, the LUMO density is important. From a physical viewpoint, the energy gap between the electronic orbitals signifies the energy required to transfer one electron from the molecular ground state to the excited state, thus, can characterize the chemical properties of the molecules. The HOMO and LUMO molecular orbitals of the compounds are shown in Fig. 2. On keen observation, the HOMO lobes are distributed mostly over the N-linked heterocyclic rings of morpholine derivatives; whereas, the LUMO lobes are almost homogeneously spread over benzimidazole ring. Favorable electron donating molecule's proclivity to the proper low-lying molecular orbital of acceptor molecule can be predicted from the high value of HOMO. From the least value of LUMO, the back-bonding tendency from the d-orbital of metal atom to an inhibitor molecule could be inferred.

Considering these explanations, it would be felicitous to compare the electronic properties. Certain quantum chemical parameters related to these molecular electronic structures have been compared with corresponding percentage values of experimental inhibition efficiencies (Table 2). The theoretical data summarized in Table 2 show that in gas phase 1-(phenyl)-1-(morpholinomethyl)-cyclohexylamine (M3) has the highest E_{HOMO}, whereas 1-(phenyl)-1-(cyclohexylaminomethyl)-benzotriazole (S4) has the lowest value. On the other hand, in aqueous phase, 1-(phenyl)-1-(morpholino-methyl) benzotriazole (S5) has the highest E_{HOMO} and morpholine (M1) has the lowest value. Furthermore, 1-(phenyl)-1-(morpho-linomethyl) benzotriazole (S5) has the lowest E_{LUMO} and ΔE values in gas and aqueous phases, however, 1-(phenyl)-1-(cyclohexylaminomethyl)benzotriazole (S4) has the lowest E_{LUMO} in aqueous phase.

To put into perspective, any attempt to correlate the calculated E_{HOMO}, E_{LUMO}, and ΔE values of the compounds with experimental inhibition efficiencies is not successful and there is no simple relation or any derived direct trend with the inhibition performance of these inhibitors. More reactive nucleophile is characterized by a lower value of ω, in opposite good electrophile is characterized by high value of ω. In this regard, dimorpholinomethane (M4) is good electrophile in both phases. Hard molecule has large energy disparity and soft molecule has small energy disparity. Soft molecules are more reactive

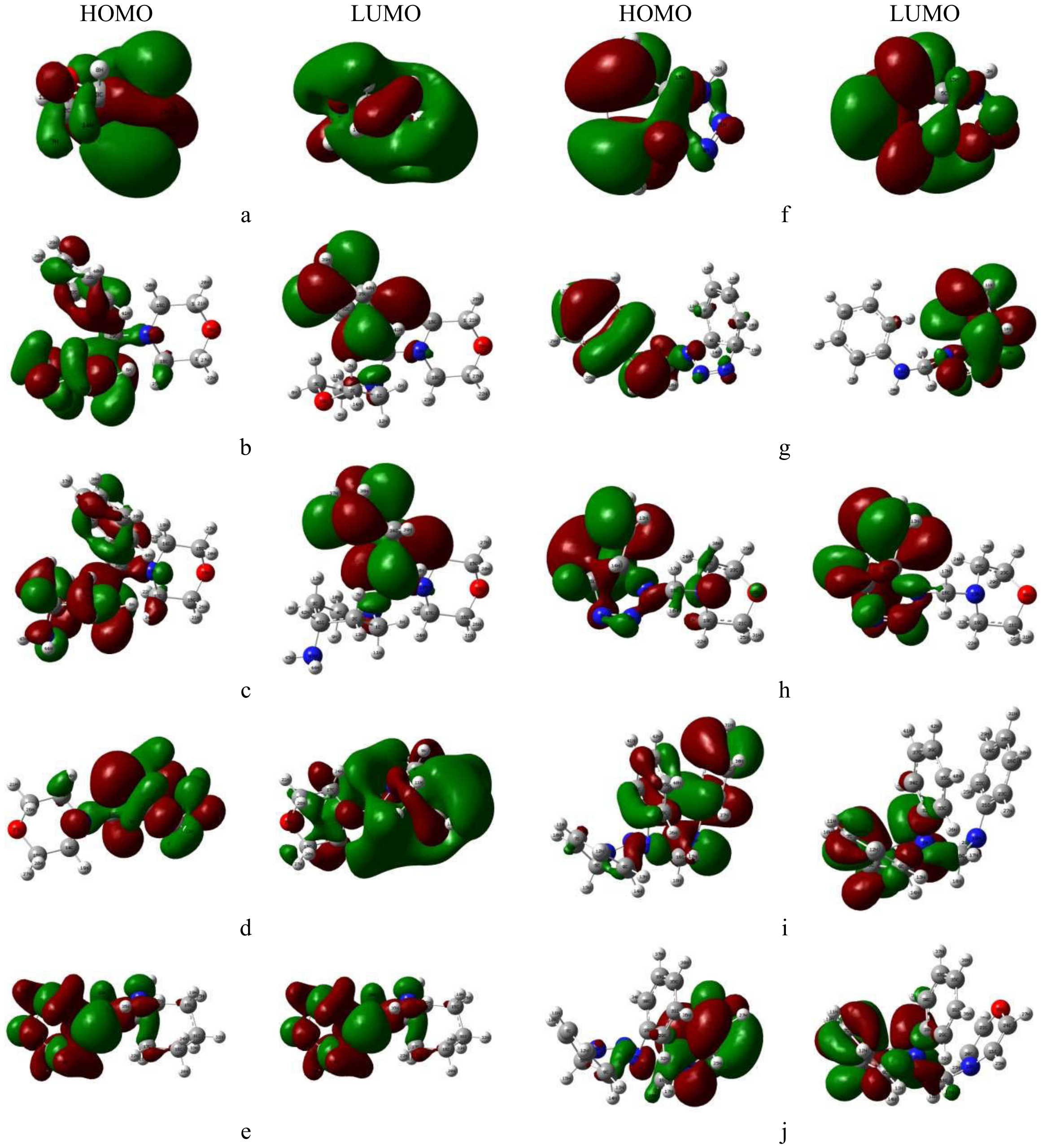

Fig. 2. Molecular orbital surfaces for HOMO and LUMO of (a) morpholine (M1), (b) dimorpholine phenylmethane (M2), (c) 1-(phenyl)-1-(morpholinomethyl)-cyclohexylamine (M3), (d) dimorpholinomethane (M4), (e) 1-morpholinomethylcyclohexylamine (M5), (f) benzotriazole (S1), (g) 1-cyclohexylaminomethylbenzotriazole (S2), (h) 1-morpholinomethylbenzotriazole (S3), (i) 1-(phenyl)-1-(cyclohexylaminomethyl)benzotriazole (S4), and (j) 1-(phenyl)-1-(morpholinomethyl) benzotriazole (S5) in aqueous phase

than hard ones because they could easily offer electrons to an acceptor. As observed, 1-(phenyl)-1-(morpholinomethyl) benzotriazole (S5) is the most soft molecule amongst the others. Hereby, the comparison of chemical hardness values also shows similar trend to those of the energy gaps, being 1-(phenyl)-1-(morpholinomethyl) benzotriazole (S5) the lowest. Again, dipole moment (μ) is another parameter, which predicts the polarized nature of the molecule although its relation to inhibition efficiency is controversial. It has been generally asserted that the efficiency of the inhibitor increases with the growth in the total dipole moment of the compound. The theoretical study has shown that 1-(phenyl)-1-(cyclohexylaminomethyl)benzotriazole (S4) in aqueous phase, albeit deprived of any

Table 2

M06-2X/DGDZVP calculated electronic properties of molecules

Parameters	Phase [b]	S1	S2	S3	S4	S5	M1	M2	M3	M4	M5
Inhibition efficiency (%)[a]		71	85	73	91	81	74	82	84	78	86
E_{HOMO} (eV)	G	–7.929	–7.069	–7.812	–10.554	–9.822	–8.061	–7.143	–6.911	–7.399	–7.006
	A	–7.767	–7.111	–7.749	–7.429	–6.703	–8.129	–7.106	–6.945	–7.406	–7.172
E_{LUMO} (eV)	G	–0.459	–0.601	–0.606	–4.643	–4.567	3.134	0.269	0.434	3.079	2.682
	A	–0.303	–0.355	–0.335	–1.143	–1.093	3.494	0.439	0.479	3.385	3.201
ΔE (E_L–E_H) (eV)	G	7.470	6.468	7.206	5.911	5.255	11.195	7.412	7.345	10.478	9.688
	A	7.464	6.756	7.414	6.286	5.610	11.623	7.545	7.424	10.791	10.373
∂ (D)	G	3.482	2.905	3.298	4.631	4.680	1.773	2.283	1.582	0.982	2.884
	A	4.837	5.382	4.715	8.411	8.278	2.283	2.087	4.823	1.631	2.509
ω	G	2.355	2.274	2.458	9.767	9.849	0.542	1.594	1.473	0.445	0.482
	A	2.181	2.063	2.204	2.965	2.836	0.462	1.473	1.408	0.375	0.380
χ	G	4.194	3.835	4.209	7.599	7.195	2.464	3.437	3.289	2.160	2.162
	A	4.035	3.733	4.042	4.317	3.898	2.318	3.334	3.233	2.011	1.986
η	G	3.735	3.234	3.603	2.956	2.628	5.598	3.706	3.673	5.239	4.844
	A	3.732	3.378	3.707	3.143	2.805	5.812	3.773	3.712	5.396	5.187
S	G	0.134	0.155	0.139	0.169	0.190	0.089	0.135	0.136	0.095	0.103
	A	0.134	0.148	0.135	0.159	0.178	0.086	0.133	0.135	0.093	0.096
ΔN	G	0.084	0.152	0.085	–0.470	–0.452	0.210	0.187	0.208	0.254	0.274
	A	0.105	0.161	0.105	0.080	0.164	0.215	0.197	0.213	0.260	0.273

[a] Ref. [9]

[b] G – gas phase (ε=1.0); A – aqueous phase (ε=78.5).

regularity, has high value of dipole moment.

During the interaction of the inhibitor molecule with bulk metal, electrons flow from the lower electronegative molecule to the higher electronegative metal until the chemical potential becomes equalized. When two systems, Fe and inhibitor, are brought together, electrons will flow from lower χ (inhibitor) to higher χ (Fe), until the chemical potentials become equal. The estimation of the fraction of the transferred electron, ΔN, for all molecules are also listed in Table 2. If $\Delta N<3.6$, the inhibition efficiency increases by increasing the electron-donating ability of these molecules to donate electrons to the metal surface. In general, a larger fraction of transferred electrons is found for morpholine derivatives, in which 1-morpholinomethylcyclohexylamine (M5) is ranked as the best. In that vein, this order again is not compatible with inhibition efficiency (%) values because no regular variation can be found between theoretical and experimental results. Based on the presented data, it has been clearly understood that for all considered cases ΔN is considerably smaller than 3.6, which was also ratified and expatiated by a recent infallible computational study [15].

Conclusions

Despite the compatibility with the experimental values given in literature that proves the conformability of the selected method and the correctness of the selected basis set for the optimization of inhibitor structures, it has been shown that none among the evaluated molecular electronic parameters (ionization potential, electron affinity, chemical hardness, electronegativity, HOMO, LUMO, HOMO–LUMO gap energies, and dipole, etc.) correlates with experimentally determined inhibition efficiency for a set of 10 Schiff and Mannich bases, tested as corrosion inhibitors for steel in neutral aqueous solution. Nonetheless, the main deduction of this study is that frequently used theoretical methods to predict the correlation between molecular electronic properties and inhibition efficiency of corrosion inhibitors with some success do not seem to capture the protection behavior of such compounds on metal surface in a corrosive environment. This result is attributed to the fact that DFT calculations are still not feasible to perform at the solid/water interface (which is indispensable in corrosion), and a convenient description of solvent and electrified interfaces is abstruse task in computational studies.

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ІНГІБУВАННЯ КОРОЗІЇ СТАЛІ ДЕЯКИМИ ОСНОВАМИ ШИФФА І МАННІХА: ТЕОРЕТИЧНЕ ОЦІНЮВАННЯ

Г. Геце

Немає сумнівів, що значення та важливість використання обчислювальних методів у науці про корозію поступово визнаються все більшою мірою. Поглиблене вивчення тези про те, що деякі молекулярні електронні параметри, такі як потенціал іонізації, спорідненість до електронів, зазор HOMO–LUMO, дипольний момент, мають значення, оскільки вони дозволяють охарактеризувати особливості дії інгібіторів корозії, призводить до подальших труднощів. Надійність таких параметрів є предметом суперечок, і, отже, дане дослідження є продовженням спроби розглянути попередні експериментальні результати, що стосується деяких основ Шиффа і Манніха як інгібіторів корозії сталі в нейтральному водному розчині за допомогою розрахунків відповідно до теорії функціонала густини. Через наявність певних джерел невизначеностей (таких як структура молекулярної моделі, опис природоохоронних зусиль та помилки, пов'язані з природою квантово-хімічних методів) було зроблено висновок, що неможливо скласти послідовну картину про властивості інгібування корозії досліджуваних сполук через обчислювані параметри.

Ключові слова: вуглецева сталь, корозія, інгібітор, основа Шиффа, основа Манніха, теорія функціонала густини.

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