Quantum chemical and molecular dynamic simulation studies for the prediction of inhibition efficiencies of some piperidine derivatives on the corrosion of iron

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ARTICLE INFO

ABSTRACT

The adsorption and corrosion inhibition properties of three piperidine derivatives namely, (1-(5-fluoro-2-(methylthio) pyrimidine-4-yl) piperidine-4-yl)-2,5-dimethoxybenzenesulfonamide (FMPPDBS), (1-(5-fluoro-2-(methylthio) pyrimidine-4-yl) piperidine-4-yl)-4-nitrobenzenesulfonamide (FMPPNBS), (1-(5-fluoro-2-(methylthio) pyrimidine-4-yl) piperidine-4-yl)-3-methoxybenzenesulfonamide (FMPPMBS) on the corrosion of iron were investigated by performing quantum chemical calculations and molecular dynamics simulations. Global reactivity parameters such as E_{HOMO}, E_{LUMO}, HOMO–LUMO energy gap (ΔE), chemical hardness, softness, electronegativity, proton affinity, electrophilicity and nucleophilicity have been calculated and discussed. The adsorption behaviors of these piperidine derivatives on Fe(110), Fe(100) and Fe(111) surfaces were investigated using molecular dynamics simulation. The binding energies on metal surface of studied compounds followed the order: FMPPDBS > FMPPMBS> FMPPNBS and this ranking obtained is consistent with the experimental data.

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1. Introduction

Iron is one of the metals used in many chemical industries because of its easy fabrication and lower cost. For these reasons, prevention of the corrosion of iron is quite important in the industry. One of the most effective alternatives for the protection of metallic surfaces against corrosion is to use organic inhibitors containing nitrogen, oxygen, sulfur and aromatic ring in their molecular structure [1–4]. Nitrogen and sulfur containing heterocyclic compounds like piperidine derivatives are known as effective corrosion inhibitors against corrosion of metallic surfaces [5,6].

Experimental techniques are very convenient in the understanding of inhibition mechanism but they are generally expensive and time-consuming. With the improvement of computer hardware and software, density functional theory (DFT) [7,8] and molecular dynamic simulation methods in recent times have become fast and powerful tools to predict the corrosion inhibition efficiencies of inhibitor molecules [9–14]. In the conceptual DFT, quantum chemical parameters such as chemical hardness [15,16], softness [17], electronegativity [18], proton affinity [19], electrophilicity [20] and nucleophilicity are considered in the prediction of chemical reactivity or stability. In the calculation of these mentioned chemical properties, Koopman's theorem [21] provides great facilities to computational and theoretical chemists. According to this theory, ionization energy and electron affinity values of chemical species are associated with their HOMO and LUMO energy values, respectively.

Hard–soft acid and base (HSAB) [22–24] principle introduced by Pearson states that "hard acids prefer to coordinate to hard bases and soft acids prefer to coordinate to soft bases." Polarizable chemical species is defined with soft concept. As can be understood from this classification of Pearson, sulfur containing structures give electrons easily to metals [25]. Thus, such molecules are effective against metal corrosion. Chemical structures of molecules considered in this study are shown in Fig. 1.

Recently, Kumar et al. [26] synthesized and investigated experimentally the inhibitive performance of the studied molecules on

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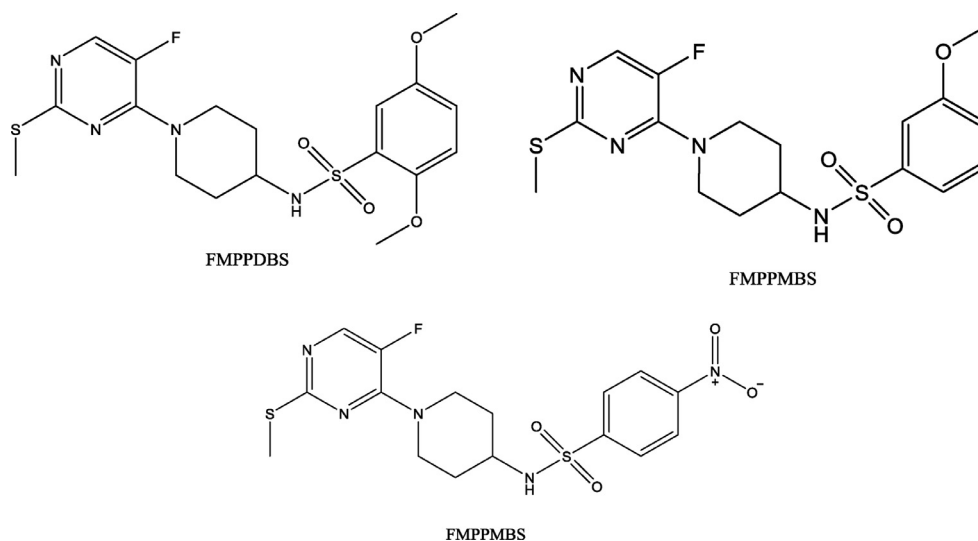 E-mail address: savaskaya@cumhuriyet.edu.tr (S. Kaya).

Fig. 1. Chemical molecular structures of studied piperidine derivatives: FMPPDBS, FMPPMBS, FMPPNBS.

the corrosion of mild steel in acidic medium. The goal of present work is to evaluate the corrosion inhibition performance of the molecules in Fig. 1 on the corrosion of iron using quantum chemical calculations and molecular dynamics simulations approach and also to determine the most effective corrosion inhibitor among them theoretically.

2. Computational details

2.1. Quantum chemical calculations

Density Functional Theory is certainly the most widely used methodology for the prediction of chemical reactivity of molecules, clusters and solids. It is important to note that DFT methods have become very popular in recent times [27]. In the present study, DFT calculations were carried out using Gaussian 9.0 Program [28]. The input files of studied molecules were prepared with Gauss View 5.0.8 [29]. A full optimization was performed up to a higher basis set denoted by 6-31G++ (d, p) because this basis set gives more accurate results in terms of the determination of geometries and electronic properties for a wide range of organic compounds. The calculations in both gas and aqueous phases were also made using other levels of theory such as HF and DFT/B3LYP methods with SDD, 6-31++G (d, p) and 6-31 G basis sets (see Fig. 2).

In the conceptual Density Functional Theory, chemical reactivity indices such as chemical hardness, electronegativity, chemical potential are defined as derivatives of the electronic energy (E) with respect to number of electrons (N) at a constant external potential, $\upsilon(r)$. Within the framework of this theory, mentioned chemical properties are given as [30,31]:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{\upsilon(r)} \tag{1}$$

$$\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{\upsilon(r)} = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(r)} \tag{2}$$

With the help of finite differences method [32], for chemical hardness, electronegativity and chemical potential, the following expressions based on first vertical ionization energy and electron affinity values of chemical species are given.

$$\eta = \frac{I - A}{2} \tag{3}$$

$$\chi = -\mu = \frac{I + A}{2} \tag{4}$$

According to Koopman's theorem [21], the negative of the highest occupied molecular orbital energy and the negative of the lowest unoccupied molecular orbital energy corresponds to ionization energy and electron affinity, respectively ($-E_{HOMO} = I$ and $-E_{LUMO} = A$). As a result of this theorem, chemical potential and chemical hardness can be expressed as [33]:

$$\mu = \frac{E_{LUMO} + E_{HOMO}}{2} \tag{5}$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \tag{6}$$

The global softness is defined as the inverse of the global hardness and this quantity is given as [17,34]:

$$S = \frac{1}{\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{\upsilon(r)} \tag{7}$$

The global electrophilicity index (ω) introduced by Parr et al. [35] is the inverse of nucleophilicity and is given below in Eq. (8). From the light of this index, electrophilic power of a chemical compounds is associated with its electronegativity and chemical hardness. Nucleophilicity (ε) is the inverse of the electrophilicity as is given below in Eq. (9) [20]:

$$\varepsilon = 1/\omega \tag{8}$$

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \tag{9}$$

2.2. Molecular dynamics simulations

The adsorption progress of three piperidine derivatives on iron surface is investigated by performing molecular dynamics simulations using Forcite module from Accelrys Inc. [36,37]. The model metal surfaces comprised of a Fe crystal cleaved along the (110), (100), and (111) plane, with a vacuum layer on the topside. It should be noted that Fe(110) is a density packed surface and has the most stabilization compared to other Fe surfaces [38]. It is important that the size of the vacuum is great enough such that the non-bonded calculation for the adsorbate does not interact with the periodic image of the bottom layer of atoms in the surface;