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ORIGINAL ARTICLE

A theoretical study on the inhibition efficiencies of some quinoxalines as corrosion inhibitors of copper in nitric acid

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Abstract Quantum chemical calculations based on DFT method were performed on three quinoxalines compounds namely ethyl 2-(4-(2-ethoxy-2-oxoethyl)-2-*p*-tolylquinoxalin-1(4*H*)-yl)acetate (*Q*1), 1-[4-acetyl-2-(4-chlorophenyl)quinoxalin-1(4*H*)-yl]acetone (*Q*2) and 2-(4-methylphenyl)-1,4-dihydroquinoxaline (*Q*3), used as corrosion inhibitors for copper in nitric acid media to determine the relationship between the molecular structure of quinoxalines and inhibition efficiency. Quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the fraction of electrons transferred (ΔN), and the total energy (TE), were calculated. The theoretically obtained results were found to be consistent with the experimental data reported.

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1. Introduction

The corrosion of metal surface is translated into great economic loss for industry, and one of the most efficient alternatives to protect metals of this phenomenon is the use of substances (inhibitors) that are adsorbed on the metallic surfaces to slow down the cathodic as well as the anodic process of dissolution on the metal (Mora-Mendoza et al., 2002).

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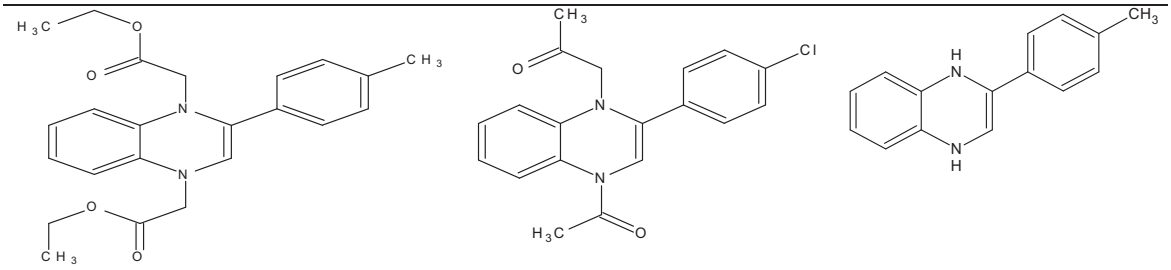

ethyl 2-(4-(2-ethoxy-2-oxoethyl)-2-*p*-tolylquinoxalin-1(4*H*)-yl)acetate **(Q1)**	1-[4-acetyl-2-(4-chlorophenyl)quinoxalin-1(4*H*)-yl]acetone **(Q2)**	2-(4-methylphenyl)-1,4-dihydroquinoxaline **(Q3)**

Figure 1 The molecular structures of the investigated inhibitors.

Because of the general aggressiveness of acid solutions, the use of inhibitors to control the destructive attack of acid environment was found to have widespread applications in many industries. The inhibition of corrosion of copper in acidic medium by organic inhibitors has been studied in considerable details (Zarrouk et al., 2010a,b,c; Khalifa et al., 2010; Khaled et al., 2009a,b; Fouda et al., 2000; Fiala et al., 2007; El-Naggar, 2000; Lee, 2003; Khodari et al., 2001). The remarkable inhibitory effect is reinforced by the presence of heteroatoms such as sulphur, nitrogen and oxygen in the ring which facilitates its adsorption on the metal surface following the sequence O < N < S (Donnelly et al., 1978; Tadros and Abd-el-Nabey, 1988; Thomas, 1980). It has been reported that N-containing inhibitors exert their best efficiencies in hydrochloric acid (Schmitt, 1984). So, the inhibition efficiency of an inhibitor depends not only on the characteristic of the environment in which it acts, the nature of the metal surface but also on the structure of the inhibitor itself which includes the number of adsorption active centers in the molecule, the charge density, the molecular size, the mode of adsorption and the formation of metallic complexes (Chetouani et al., 2005). Among the various nitrogenous compounds studied as inhibitors, quinoxalines have been considered as environmentally acceptable chemicals. Many substituted quinoxaline compounds have been recently studied in considerable details as effective corrosion inhibitors for steel and copper in acidic media (Zarrouk et al., 2010a,b,c; El Ouali et al., 2010; Benabdellah et al., 2007; Obot and Obi-Egbedi, 2010a,b; Obot et al., 2010).

On the other hand, several quantum chemical methods and quantum-chemistry calculations have been performed in order to study the molecular structure and the reaction mechanisms in order to interpret the experimental results as well as to solve chemical ambiguities and to correlate the inhibition efficiency to the molecular properties of this type of compounds ().

The structure and electronic parameters can be obtained by means of theoretical calculations using the computational methodologies of quantum chemistry. The geometry of the inhibitor in its ground state, as well as the nature of their molecular orbitals, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are involved in the properties of activity of inhibitors.

The relationships between the structural parameters and corrosion inhibition of those compounds have not been studied yet. The objective of this work is to calculate the most relevant molecular properties on its action as inhibition of the corrosion of three quinoxalines compounds. These properties are the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the fraction of electrons transferred (ΔN), and the total energy (TE). Fig. 1 represents the investigated inhibitors: ethyl 2-(4-(2-ethoxy-2-oxoethyl)-2-*p*-tolylquinoxalin-1(4*H*)-yl)acetate ($Q1$), 1-[4-acetyl-2-(4-chlorophenyl)quinoxalin-1(4*H*)-yl]acetone ($Q2$) and 2-(4-methylphenyl)-1,4-dihydroquinoxaline ($Q3$).

2. Theory and computational details

DFT (density functional theory) methods were used in this study. These methods have become very popular in recent years because they can reach exactitude similar to other methods (ab initio, QSAR: Quantitative Structure–Activity Relationships,...) in less time and are cheaper from the computational point of view. In agreement with the DFT results, energy of the fundamental state of a polyelectronic system can be expressed through the total electronic density, and in fact, the use of electronic density instead of wave function for calculating the energy constitutes the fundamental base of DFT. All calculations were done by GAUSSIAN 03 W software (Frisch, 2003), using the B3LYP functional (Zhang et al., 2005; Lashgari et al., 2005) and a 6-31G* basis set (Lashgari et al., 2005). The B3LYP, a version of DFT method, uses Becke's three-parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang, and Parr (LYP) (Zhang et al., 2005; Lashgari et al., 2005). The geometry of all species under investigation was determined by optimizing all the geometrical variables without any symmetry constraints. Frontier molecular orbitals (HOMO and LUMO) may be used to predict the adsorption centers of the inhibitor molecule. For the simplest transfer of electrons, adsorption should occur at the part of the molecule where the softness,