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## Quantum chemical studies on the some inorganic corrosion inhibitors

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## ABSTRACT

Some quantum chemical parameters were calculated by using Hartree–Fock (HF) approximation, Density Functional Theory (DFT/B3LYP) and Møller Plesset perturbation theory (MP3) methods at LANL2DZ, LANL2MB and SDD levels in gas phase and water for dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ), chromate ( $\text{CrO}_4^{2-}$ ), tungstate ( $\text{WO}_4^{2-}$ ), molybdate ( $\text{MoO}_4^{2-}$ ), nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ) which are used as inorganic corrosion inhibitors. All theoretical results and experimental inhibition efficiencies of inhibitors were subjected to correlation analyses. In a summary, MP3/SDD level in water was found as the best level. In this level, the inhibition efficiency ranking was found as  $\text{CrO}_4^{2-} > \text{WO}_4^{2-} > \text{MoO}_4^{2-} > \text{Cr}_2\text{O}_7^{2-} > \text{NO}_2^- \approx \text{NO}_3^-$ .

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## 1. Introduction

Corrosion mechanism and corrosion prevention has been receiving wide attractions [1–5]. The corrosion of metal surface causes in a great economic loss for industry and one of the alternative ways of the metal protection is to use the inhibitors [6]. Many oxyanions such as dichromates, chromates, tungstates, molybdates, nitrites and nitrates have been used as corrosion inhibitors [7–19]. These inhibitive anions are powerful oxidizing agents. They have other important roles such as chelating agent and abrasive particle. The effectivities of some corrosion inhibitors depend upon the type of material, its properties and the corrosion environment [12,20]. For instance, inhibition efficiency of molybdate anion increases with the increasing of oxygen concentration in corrosion environment [13,14]. Some of these anions have been used satisfactorily in many corrosive environment. For instance, molybdates have been used to prevent mild steel corrosion [21] and cold rolling steel corrosion [22] in simulated cooling water, in zinc corrosion inhibition [23], on bacterial corrosion and iron [20]. Nitrates have been used to prevent galvanized steel, aluminum corrosion [20], zinc corrosion in NaCl solution [23,24], on the pit initiation of pure aluminum in HCl solution [25] and in sol–gel coatings for steel [26]. Chromates are very effective corrosion inhibitor for iron and ferrous alloys in the presence of halide ions [15]. This effect is explained with oxidation of iron.

There are many experimental study on inhibition efficiency of inorganic inhibitors [7–19,27–30]. Five experimental studies were selected to explain the inhibition efficiency as theoretically. The first experimental study was performed by Zhao and Zuo [16]. The role of molybdate and dichromate anions on pitting growth

of mild steel in bicarbonate solution containing  $\text{Cl}^-$  anion were investigated [16]. According to their report, molybdate anion was more effective than dichromate. The second experimental study was made by Ilevbare and Burstein [17]. The effect of chromate and molybdate anions on embryonic stages of pitting corrosion and on stable pitting were examined [17]. Their report indicates that chromate is better inhibitor than molybdate under the experimental conditions. The third study was made by Foad El-Sherbini [18]. The effect of tungstate, molybdate and nitrite anions on pitting corrosion in sodium carbonate solution containing perchlorate were investigated [18]. The inhibitive effects of these anions decrease in the following order [18]:



The fourth study was made by Foad El-Sherbini et al. [19]. The effect of tungstate, molybdate and nitrite anions on corrosion of tin in sodium borate solution containing halides ions were examined [19]. The effects of these inorganic anions decrease in the following order [19]:



The inhibition efficiency of  $\text{CrO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$  and  $\text{NO}_3^-$  against 1018 carbon steel in the LiBr + ethylene glycol +  $\text{H}_2\text{O}$  mixture were obtained at 5, 20, 50 ppm of inhibitors with electrochemical techniques, which are potentiodynamic polarization curves, electrochemical noise resistance and electrochemical impedance spectroscopy measurements. These results were reported by Samiento-Bustos et al. [15]. The best inhibition efficiencies of these inhibitors were obtained at 20 ppm. According to the study of Samiento-Bustos et al. there is an agreement between inhibition efficiencies which are obtained with electrochemical noise resistance and electrochemical impedance spectroscopy measurements. The inhibition efficiencies decrease in the following order [15]:

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The prevailing environmental conditions would usually determine the mechanism of the inhibitor action [20]. Many mechanism have been used to explain the action of inorganic inhibitors. The primary step in the mechanism of inhibitors in acid solution is generally accepted as the adsorption of the inhibiting species onto the metal surface [12,13,31,32].

Some quantum chemical studies about corrosion inhibition efficiency have been successfully performed and the molecular properties were explained for different kinds of corrosion inhibitors [33–38]. We focused on the six oxyanions ( $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ ) to determine the theoretical inhibition efficiency. The highest occupied molecular orbital energy ( $E_{\text{HOMO}}$ ), the lowest unoccupied molecular orbital energy ( $E_{\text{LUMO}}$ ), the energy gap ( $\Delta E_{\text{HOMO-LUMO}}$ ), sum of total negative Mulliken charges (TNC1), sum of total negative natural bond orbital (NBO) charges (TNC2), hardness ( $\eta$ ), softness ( $\sigma$ ), proton affinities (PA), molecular volume ( $V$ ) and molecular orbital character analyses were calculated by using HF, DFT, MP methods with different basis sets in gas phase and water. The appropriate method and basis sets were selected. Correlations between the experimental inhibition efficiencies and quantum chemical parameters were investigated. The inhibition efficiencies of all inhibitors were compared with each other.

## 2. Calculation method

The input files of inorganic inhibitors were prepared with GaussView 5.0.8 [39]. All calculations were made by using Gaussian 09 Revision-A.02 [40] and Gaussian 09 AML64L-Revision-C.01 [41]. All molecules were fully optimized by using HF, DFT/B3LYP and MP3 methods with LANL2DZ [42], LANL2MB [43], SDD [44] basis sets in gas phase and water. The Hartree–Fock (HF) approximation for the total interacting system is taken as the zero-order approximation. The B3LYP combination of exchange and correlation functional [45,46] in DFT is applied to all the electronic structure calculations. The third-order MP (MP3) theory can be a straightforward option by the perturbational inclusion of electron pair–pair interactions [47,48]. LANL2DZ, LANL2MB and SDD are basis sets for post-third-row atoms. They use effective core potentials in calculations [49]. The interactions of solute–solvent were taken into account by the conductor-like polarizable continuum model (CPCM). According to this model, the solute molecule is placed into a cavity surrounded by the solvent considered as a continuum medium of a certain dielectric constant. The charge distribution of the solute polarizes the dielectric continuum, which creates an electrostatic field that in turn polarizes the solute [50]. The vibrational frequency analyses indicate that optimized structures of all inhibitors are at stationary points corresponding to local minima without imaginary frequencies.

Frontier molecular orbitals can be used to predict the adsorption centers of the inhibitors. The adsorption center is depended on different parameters of inhibitors. According to theorem of Koopman, the  $E_{\text{HOMO}}$  of the inhibitor molecule is related to ionization potential ( $I$ ) Eq. (1) while  $E_{\text{LUMO}}$  is related to electron affinity ( $A$ ) Eq. (2) [10]:

$$I = -E_{\text{HOMO}} \quad (1)$$

$$A = -E_{\text{LUMO}} \quad (2)$$

Absolute hardness ( $\eta$ ) of the inhibitor molecule are given by Eq. (3) [51]:

$$\eta = \frac{I - A}{2} \quad (3)$$

The softness of inhibitor molecules are the inverse of absolute hardness.

## 3. Result and discussion

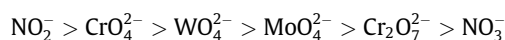
### 3.1. Non-protonated inhibitors

Quantum chemical calculations were performed to investigate the inhibition efficiencies of mentioned inhibitors. The optimized molecular structures of non-protonated inhibitors were represented in Fig. 1.

$E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ ,  $\Delta E_{\text{LUMO-HOMO}}$ , TNC1, TNC2,  $\eta$ ,  $\sigma$  and  $V$  were obtained by using HF, DFT and MP3 methods with different basis sets both gas phase and water. The results were listed in Tables 1–3 for HF, DFT and MP3 methods, respectively.

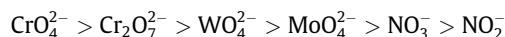
Compared with quantum chemical parameters in Table 1 and inhibition efficiencies of inorganic inhibitors, it can be seen that the results in water are more appropriate than the gas phase at HF method. The results at HF/SDD level in water are more appropriate with experimental results than other calculated results. Therefore the results at HF method with SDD basis set in water were interpreted in following.

$E_{\text{HOMO}}$  is a quantum chemical descriptor and usually associated with electron donating ability of molecule. High value of  $E_{\text{HOMO}}$  indicates the tendency of electron transfer to low empty molecular orbital of appropriate acceptor molecule. If the energy of HOMO is decisive for the inhibitor properties, the ranking of the compounds should be:



There is an agreement between the  $E_{\text{HOMO}}$  ranking at HF/SDD level in water and experimental results which are studied by Samiento-Bustos et al. [15], Zhao and Zuo [16] and Ilevbare and Burstein [17].

The low  $E_{\text{LUMO}}$  value indicates that the electron accepting ability of the molecule is higher [10,51]. The binding ability of inhibitor to metal surface increases with increasing of the HOMO and decreasing of the LUMO of inhibitors. If the energy of LUMO is decisive for the inhibitor properties, the ranking of the compounds should be:



The theoretical results at HF method with SDD basis set are in agreement with the results reported by Samiento-Bustos et al. [15], Ilevbare and Burstein [17], Foad El-Sherbini [18] and Foad El-Sherbini et al. [19].

The LUMO–HOMO energy gap ( $\Delta E$ ) is an important parameter as a function of reactivity of the inhibitor molecule towards the

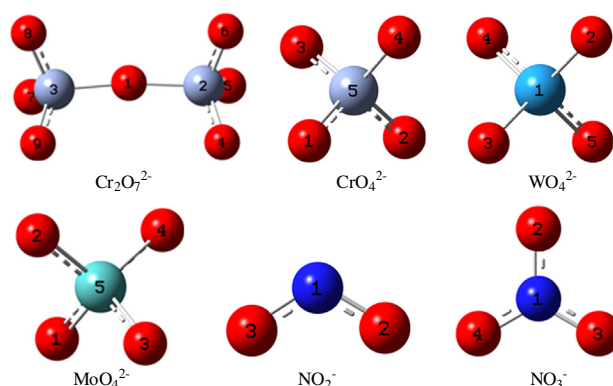


Fig. 1. Optimized molecular structure and numbering of atoms for non-protonated inhibitors at MP3/SDD level in water.

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