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# Theoretical Investigation of Corrosion Inhibition of Iron Metal by Some Benzothiazole Derivatives: A Monte Carlo Study

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**Abstract:** It is important to note that atomistic modeling and simulations are becoming increasingly popular in the field of corrosion inhibition of metal surfaces. In this work, we investigated the adsorption properties and corrosion inhibition efficiencies of some benzothiazole derivatives (ABT, TCHBT, TSCBT) against the corrosion of iron metal using molecular dynamics simulation approach. It is important to note that adsorption and binding energies calculated considering adsorption processes on Fe metal surface of aforementioned inhibitory molecules are in good agreement with experimental data reported earlier.

**Keywords**: Molecular Modeling; Monte Carlo; Benzothiazole; Metal Protection; Corrosion Inhibitors.

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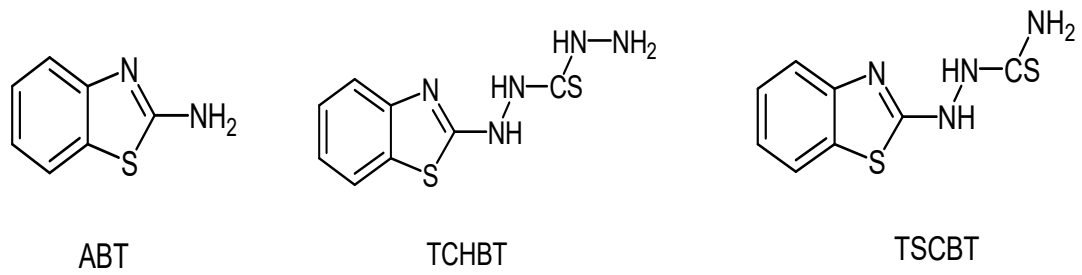
## INTRODUCTION

Corrosion can be defined as an undesirable process that causes destruction of the metal surfaces (1). Nowadays, corrosion inhibition study is a very active field of research. It is important to note that iron and copper metals are widely used in industry and the corrosion of such metals is one of the reasons of great economic losses worldwide (2). One of the most common approaches considered to protect the metal surfaces from corrosion is to use corrosion inhibitor. A corrosion inhibitor is a chemical compound which, when added in small concentrations to an environment, minimizes or prevents corrosion (3).

Many researchers noted that most effective corrosion inhibitors are π-systems and heterocyclic compounds (4, 5). For that reason, organic inhibitors containing heteroatoms like nitrogen, oxygen, sulfur, and aromatic ring in their molecular structure are very effective in terms of the prevention of the corrosion of metal surfaces. Experimental corrosion analysis techniques are widely considered to elucidate the corrosion inhibition mechanisms and to analyze the corrosion inhibition efficiencies of new synthesized compounds, but they are generally expensive and time-consuming. Recently, to predict the corrosion inhibition efficiencies of molecules, quantum chemical and molecular dynamics simulation approaches are preferred by theoretical chemists because of their speed and usability (6).




ABT TCHBT TSCBT

**Figure 1:** Molecular structures of studied benzothiazole derivatives.

In Figure 1, the molecular structures of considered molecules in this study are given. In the current literature, many benzothiazole derivatives reported as photostabilizers, metal complexing agents and non-toxic compounds. In 2012, Parameswari (7) and coworkers synthesized some benzothiazole derivatives, namely (benzothiazole-2-amine (ABT), benzothiazole-2-yl-thiocarbohydrazide (TCHBT) and benzothiazole-2-yl-thiosemicarbazide (TSCBT) and investigated their anticorrosive performances for mild steel in acidic medium by weight loss, potentiodynamic polarization and AC-impedance techniques. As a result of these studies, the authors obtained the experimental inhibition efficiency order for mentioned molecules as: TCHBT > TSCBT > ABT.

The objective of this work is to study the influence of the molecular structure on the inhibition of iron corrosion with the help of molecular dynamics simulations approach and to make a comparison with experimental data and theoretical data obtained in this study.

## COMPUTATIONAL DETAILS

The interaction analysis between studied benzothiazole derivatives and Fe (110) surface were made with the help of molecular dynamics simulation approach and utilizing Forcite module from Accelrys, Inc (8). As model metal surface, Fe (110) surface was considered because in general this surface is preferred in the Monte Carlo studies including theoretical investigations about the adsorption on Fe metal of various organic molecules. Adopting the adsorption locator code applied in the Material Studio 8.0 software from Biovia-Accelrys Inc. USA, simulations were performed. To simulate the all molecules and metal-inhibitor systems, COMPASS (condensed phase optimized molecular potentials for atomistic simulation studies) force field was used. The simulations of the benzothiazole derivative labeled as ABT, TSCBT and TCHBT on iron surface were carried out to determine the low energy adsorption sites of these molecules. All simulations made in the study were performed in an NVT canonical ensemble at 298 K with a time step of 1.0 fs and a total simulation time of 1000 ps by providing via the Andersen thermostat the temperature control. In the calculations, vacuum media was preferred and five layers of Fe atoms were used.

Adsorption energy provides important clues about the power of the interaction between inhibitor molecule and metal surface. To calculate the adsorption energies between inhibitor molecules and Fe (110) metal surface, corrosion scientists use the following equation (9).

$$E_{\text{ads}} = E_{\text{complex}} - \left( E_{\text{Fe}} + E_{\text{inh}} \right) \quad (1)$$

In Eq. 1, $E_{complex}$ is the total energy of an inhibitor molecule and the metal surface system. $E_{Fe}$ is described as the energy of Fe surface without adsorption of any inhibitor molecule and $E_{inh}$ represents the energy of isolated inhibitor molecules. As is known, the binding energy ($E_{binding}$) is considered as the negative value of the adsorption energy and is calculated via following equation (10, 11).

$$E_{binding} = -E_{ads} \quad (2)$$

## RESULTS AND DISCUSSION

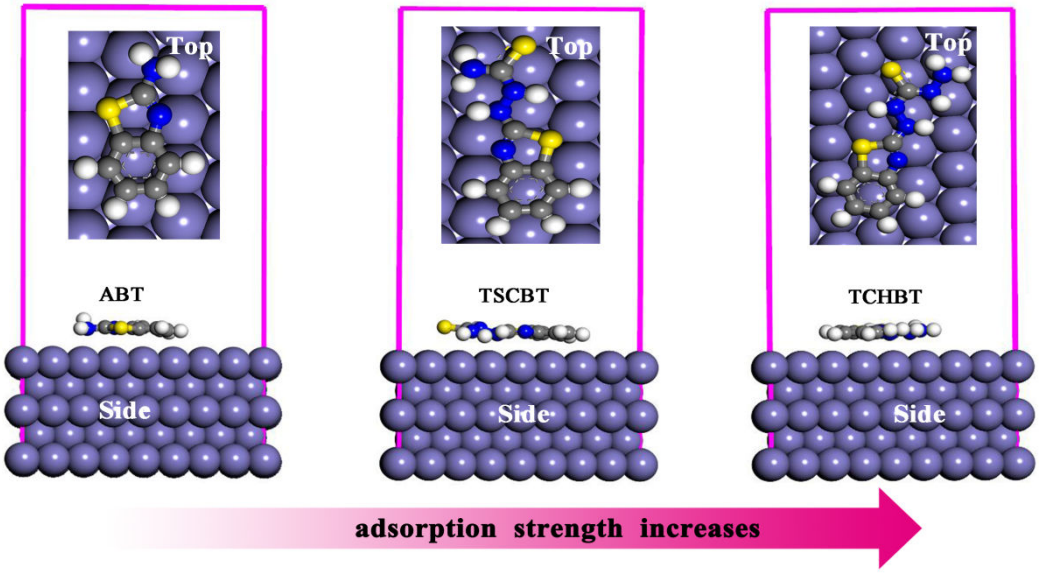



**Figure 2.** Representative snapshots of ABT, TSCBT, and TCHBT on Fe(110) surface (inset images show the on-top views).

**Table 1.** Adsorption and binding energies of three inhibitors adsorbed on Fe(110) surface.

| Systems | $E_{ads}$ (kJ mol$^{-1}$) | $E_{binding}$ (kJ mol$^{-1}$) |
|---|---|---|
| **Fe(110) + ABT** | −352.9 | 352.9 |
| **Fe(110) + TSCBT** | −482.9 | 482.9 |
| **Fe(110) + TCHBT** | −494.0 | 494.0 |

In Table 1, adsorption and binding energies calculated between Fe (110) surface and three benzothiazole derivatives using Molecular dynamics simulations approach are given. Adsorption energy is defined as the energy released when inhibitor molecule was adsorbed on metal surface. As mentioned above, the binding energy is the negative value of the adsorption energy. The most stable low energy configurations for the adsorption of ABT, TSCBT and TCHBT molecules on Fe (110) in vacuum obtained are presented in Fig. 2. It is apparent from the molecular structures of studied benzothiazole derivatives; these molecules contain a number of lone pair electrons on N and S atoms as well as π-aromatic systems. For that reason, giving the lone pair electrons on heteroatoms to the unoccupied d orbitals of iron metal, mentioned molecules can form a stable coordination bonding. It can be noticed from Fig. 2, all of the benzothiazole derivatives are adsorbed nearly parallel to the Fe (110) surface with the help of the donation of π electrons of the rings appearing in the structures of the molecules and the lone pair of the heteroatoms.

It was reported in many studies that the primary mechanism of the interaction between corrosion inhibitors and metallic iron is by adsorption. Therefore, the adsorption energies calculated via molecular dynamics simulations approach can provide us a direct tool to compare the anticorrosive performances of inhibitor molecules. It is seen from the Table 1 that the calculated adsorption energies of the studied inhibitors on iron surface are -352.9, -482,9 and -494.0 for ABT, TSCBT and TCHBT molecules, respectively. All adsorption energies are negative and these negative values which denote that the adsorption happening between metal and inhibitors could occur spontaneously. The largest negative adsorption energy represents that the system is most stable and adsorption is very strong. On the other hand, positive and larger value of the binding energy implies the corrosion inhibitor combines with Fe (110) surface more easily and tightly (10). According to calculated adsorption and binding energies for studied benzothiazole derivative, corrosion inhibition efficiencies of mentioned molecules against the corrosion of iron metal follow the order: TCHBT > TSCBT > ABT. This ranking obtained via molecular dynamic simulation approach is same with experimentally observed result. This ranking obtained can be explained in terms of the molecular structures of studied benzothiazole derivatives. π-conjugated systems and molecules having many heteroatoms in their structures are more easily adsorbed on metal surfaces and exhibit higher inhibition efficiency. It is clear from the molecular structures given via Fig. 1 that TCHBT contains good number of heteroatoms with conjugated aromatic rings in its structures compared to others. For that reason, this molecule is the best corrosion inhibitor among studied benzothiazole derivatives.

## CONCLUSION

In the present study, molecular simulation approach was employed to evaluate the corrosion inhibition performances against the corrosion of iron metal with some benzothiazole derivatives. The calculated adsorption and binding energies showed that ABT, TCHBT, TSCBT molecules are good corrosion inhibitors against the corrosion of iron. All the values of the adsorption energies are negative and these negative values are evidences of a spontaneous and strong adsorption process. Side chains appearing in the molecular structures of studied benzothiazole derivatives are very important the adsorption on Fe surface of these molecules. As results, the results obtained theoretically in this study are in good agreement with experimental data reported earlier.

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