DFT and electrochemical studies of tris(benzimidazole-2-ylmethyl)amine as an efficient corrosion inhibitor for carbon steel surface

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Abstract

The corrosion inhibition properties of tris(benzimidazole-2-ylmethyl)amine (TBMA) were analyzed by DFT and electrochemical techniques such as polarization curves and electrochemical impedance spectroscopy (EIS). DFT results clearly show that TBMA posses corrosion inhibition properties by having a delocalization region ($N_1\!=\!C_2\!=\!N_3$) in the benzimidazole ring that gives up their π electron density through its HOMO orbital to the metal LUMO to form a adsorption layer over the metallic surface; this has been proved by interacting the TBMA and its protonated structures with the surface of Fe_{13} cluster, showing that the protonated moiety adsorbs strongly on the iron surface than that of the neutral structure. Electrochemical impedance data demonstrate that the interface between the electrode and the TBMA solution decreases the charge capacitance and simultaneously increases the function of the charge/discharge of the interface, facilitating the formation of adsorption layer over the iron surface.
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Keywords: A. Benzimidazole; C. Corrosion inhibition; B. DFT; B. Impedance; A. Fe_{13} cluster

1. Introduction

There is a continuing effort to find a corrosion inhibitor that exhibits a greater effect with a smaller quantity in the corrosion medium. This is a challenging problem in the steel industry because corrosion over mild steel surfaces affects long term industrial projects [1–5]. The performance of the corrosion inhibitors based on organic compounds containing nitrogen, sulfur and oxygen atoms shows promising results. However, the stability of the inhibitor film formed over the metal surface depends on some physico-chemical properties of the molecule, related to its functional groups, aromaticity, the possible steric effects, electronic density of donors, type of the corrosive medium and nature of the interaction between the π-orbital of inhibitors with the d-orbital of iron [3–7].

Recently, density functional theory (DFT) has been used to analyze the characteristics of the inhibitor/surface mechanism and to describe the structural nature of the inhibitor on the corrosion process [8–21]. Furthermore, DFT is considered a very useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data. In previous studies [7], the compounds containing benzimidazole groups have been shown to be competent corrosion inhibitors in acid medium and this accounts for their applicability in the petroleum industry, mostly in boiler cleaning and heat exchangers [3–5,22–25]. The search an inhibitor that effectively prevents corrosion in acid medium is an attractive topic in recent days; thus, the present study is to evaluate the anti-corrosion behavior of tris(benzimidazol-2-ylmethyl)amine (TBMA) by electrochemical

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techniques, and to analyze the impact of its structural and electronic properties over iron surface by DFT.

2. Experimental procedure

2.1. Synthesis of tris(benzimidazol-2-ylmethyl)amine (TBMA)

This compound was prepared as described in the literature [26,27]. Triamino acetic acid (17.8 g, 1.0 mM) and *o*-phenylenediamine (21.6 g, 3.0 mM) were refluxed (24 h) in 6 N hydrochloric acid (80 mL). The resulting solution was allowed to cool and the green crystals obtained were collected and washed with 2 N hydrochloric acid. The free base was isolated by suspending the hydrochloride in water and neutralizing with ammonia. It was re-crystallized from aqueous ethanol and dried over P_4O_{10}. Yield 80%.

2.2. Electrochemical studies of corrosion inhibition

The electrochemical studies were carried out by a potentiostat/galvanostat instrument (Princeton Applied Research, PARC-model 273A) with a Lock-in-Amplifier (PARC-Model 5210) controlled by a computer. A cell was assembled with a carbon steel working electrode (WE) with surface area of 1.0 cm^2, two-graphite rods as counter electrodes (CE), and a saturated calomel electrode (SCE) as the reference electrode. The carbon steel composition was as follows: wt%: 0.18 C, 0.35 Mn, 0.17 Si, 0.0025 S, 0.03 P and the remainder was Fe. Prior to exposure in the corrosive medium, it was polished with 600-grit silicon carbide (SiC) paper and then rinsed with ethanol. Doubly distilled water and analytical grade hydrochloric acid, 0.5 M HCl, were used to prepare the test solutions, which were de-aerated by means of nitrogen during a period of 45 min. All the experiments were performed at static conditions and room temperature.

Polarization curves were recorded potentiodynamically only after 4.0 h of the electrode exposure to HCl (0.5 M) at a rate of 1.0 mV/s in the range −900 mV to 100 mV with respect to a standard calomel electrode (SCE). Impedance data were collected every 1 h for the time interval of total 4.0 h over a frequency range of 10,000–0.025 Hz after dipping the working electrode into HCl (0.5 M) solution containing the inhibitor. The peak-to-peak perturbation at the open-circuit potential, E_{corr} with respect to a SCE was 10 mV.

2.3. Computational details

Calculations were performed by means of the Gaussian03 program [28] for TBMA, $TBMAH^+$, $TBMAH_2^{2+}$ and $TBMAH_3^{3+}$ to analyze their electron density distribution over the structures. The bond distances obtained for the structures were similar to those reported [29] by neutron diffraction techniques, i.e. the average values were 1.32 ± 0.011 (C=N) and 1.37 ± 0.010 (C–N) where carbon

C(2) presents sp^2 hybridization. Exchange and correlation calculations were carried out with the functional hybrid B3LYP [30,31] and the 6-31G** orbital basis sets for all atoms. In all cases, total structure optimization together with the vibrational analysis of the optimized structures was carried out in order to determine whether they corresponded to a maximum or a minimum in the potential energy curve. Structural and electronic parameters of TBMA and its protonated structures were calculated by molecular orbital theory. In addition, the interaction of TBMA with iron cluster (Fe_{13}) was studied by DFT to illustrate the mechanism of ligand inhibition over the metal surface. However, the optimization of TBMA containing three methylbenzimidazole groups with Fe_{13} was unsuccessful due to the fact that a huge ligand complex structure with Fe_{13} cluster was generated and it destabilized the calculation process; therefore, the different forms of TBMA structure, *viz.*, one arm benzimidazole or two arms benzimidazoles has been substituted by methyl group to simplify the calculation process and analyzed how the electronic and structural parameters of ligand are altered when the ligand is adsorbed on the iron cluster surface.

The chemical reactivity was analyzed by frontier molecular orbital theory, Mulliken charges and the electrostatic potential map. For all the molecular structures, the possible sites of nucleophilic or electrophilic reactions with metallic surfaces were traced out by applying the electrostatic potential map. The molecular orbitals (HOMO−1 HOMO and LUMO) analysis of the present compound shows that TBMA is a potential corrosion inhibitor. HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital; HOMO−1 = next to the highest HOMO occupied molecular orbital.

3. Results and discussion

3.1. Structural and electronic properties

Applying a molecular model to calculate the electronic properties of the corrosion inhibitors to explain their action becomes vital in the corrosion process. Generally, the molecules that contain a hetero atom with a delocalization region usually posses corrosion inhibition properties. In the present work, the electronic and structural properties of TBMA were analyzed; for example, the optimizations of TBMA with H^+, $2H^+$, and $3H^+$ (Figs. 1a and b) in the gaseous state and also in solution (MeOH) state were analyzed. It is well known that the phenomena of electrochemical corrosion appear in the liquid phase, and for this reason it is necessary to include in the computational calculations the effect of a solvent. In a similar way it is important to take into account the effects that can appear as much in the geometric properties as in the electrical ones. In the GAUSSIAN 03 program, self-consistent reaction field (SCRF) methods are used to perform calculations in solution. These methods model the solvent as being continuous of uniform dielectric constant ($\varepsilon = 32.63$) and the sol-