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Experimental and theoretical investigations on the inhibition of mild steel corrosion in the ground water medium using newly synthesised bipodal and tripodal imidazole derivatives

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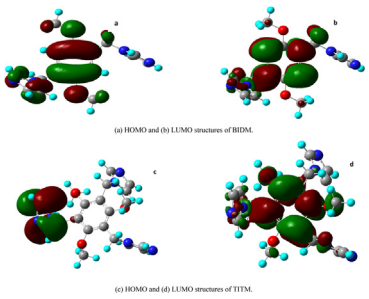
HIGHLIGHTS

- Synthesis of new imidazole derivatives-BIDM(bipodal) and TITM(tripodal) inhibitors.
- Gravimetric analysis to investigate mild steel corrosion inhibition in ground water.
- Electrochemical characterizations to substantiate results of weight loss method.
- Quantum studies to analyse the chemical behavior, structure and substituent effect.

GRAPHICAL ABSTRACT



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ABSTRACT

Two new imidazole derivatives, namely 1,4-bis(*N*-imidazolylmethyl)-2-5-dimethoxybenzene (BIDM) and 1,3,5-tris(*N*-imidazolylmethyl)-2,4,6-trimethoxybenzene (TITM), were synthesised and their effects on the inhibition of mild steel corrosion in ground water medium are reported. The study was carried out using gravimetric and electrochemical techniques in order to determine the corrosion inhibition efficiencies of the bipodal and tripodal structured imidazoles. Further, the quantum chemical calculations using density functional theory (DFT) gave a profound insight into the inhibitory action mechanism of BIDM and TITM and their calculation parameters, such as E_{HOMO}, E_{LUMO} and ΔE were in good agreement with the results of the experimental studies. BIDM and TITM exhibited lowest corrosion current densities of circa 7.5 μA cm^{-2} and 4.1 μAcm^{-2} at the optimum concentrations of 0.67 and 0.49 mM, respectively. All measurements thus confirmed that both BIDM and TITM behaved as good inhibitors for mild steel corrosion in ground water medium.

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1. Introduction

Mild steel possesses good mechanical properties and it is a better economic alternative to its low cost [1]. Hence, it finds a wide industrial application as constructional materials in acid cleaning baths, water cooling systems, different refinery units pipelines, chemical operations, steam generators, ballast tanks, oil and gas production units [2–4]. On the other hand, the mild steel is easily prone to corrosion thereby, raised an intense desire to seek for an efficient corrosion inhibitor for this metal without any toxication of waterways in all water systems and industrial concerns.

Among the different corrosion prevention and protection methods [5–7], the use of chemical inhibitors is one of the best known methods of corrosion protection. Although there are continuing advances in the formulation of corrosion resistant materials, the uses of chemical inhibitors often remain the most practical and cost effective measures of preventing corrosion [1]. In precise, the efficiency of the inhibitors mainly depends on the nature of the metal surface, the structure of the inhibitor, which includes the number of adsorption active centres in the inhibitor molecule, their molecular size and the mode of adsorption [8–11].

Corrosion inhibitors are commonly, organic compounds with hetero atoms such as N, S, P, O, unsaturated bonds and aromatic planar cycles, which may aid to accept or donate electrons in order to get adsorbed on metallic surfaces by electrostatic interactions, interaction between the unshared pair of electrons of corrosion inhibitor and metal and interaction of electrons with metallic surface [12–21]. Among the several classes of heterocyclic compounds, imidazole derivatives were found as better inhibitors against corrosion for many metals and alloys in the ground water as well as other media.

In precise, the inhibition is assumed to occur via adsorption of the compound on the steel surface through active centres present in the molecule [17,22–24]. Thus the relationship between the adsorption of organic inhibitors, their molecular structure and enhancement in corrosion resistance related to the presence of the substituted groups has attracted the curiosity of many researchers [25–29]. The quantum chemical approach used in calculating the electronic properties of the imidazole molecule also ascertained the relation between inhibiting effect and molecular structure as the increased electron density around the inhibitor molecules through substitution have paved the way for improved inhibition efficiency.

Different electrochemical techniques such as open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were usually employed to evaluate the inhibition mechanism for many decades. Whereas nowadays, a perfect exploration is attained with theoretical studies such as quantum chemical methods and molecular modelling techniques whose theoretical parameters obtained from the advanced hardware and software account for the molecular structure, reactivity, shape, binding properties and also mechanism of action in terms of chemical reactivity.

Thus the objective of the present work is to investigate the inhibition performance of the newly synthesised bipodal and tripodal imidazoles in preventing mild steel corrosion in the ground water environment. Ascertaining the corrosion inhibition on mild steel was done at different concentrations of BIDM and TITM by gravimetric analysis along with that of adsorption phenomenon and the results were correlated with that of the electrochemical techniques. Quantum chemical calculations were successively carried out to obtain the invaluable quantum chemical parameters such as E_{HOMO} and E_{LUMO} to understand the adsorption properties with respect to the structure of every individual molecule to attain a clear view on the relationship between the substituent effect and inhibition efficiency as well as molecular reactivity.

2. Materials and methods

2.1. Materials

Tests were performed on the mild steel samples (99.99% purity) of the following chemical composition (wt.%): C-0.13, P-0.032, S-0.025, Si-0.014, Mn-0.48 and Fe-balance. Specimens used in the weight loss experiment were mechanically cut into 4.0 cm × 2.0 cm × 0.2 cm dimensions. For electrochemical studies, specimens of size 1.0 cm × 1.0 × cm × 0.3 cm were cut, embedded in epoxy resin and mechanically ground with silicon carbide papers (from grades 120–1200) then followed by washing with double distilled water, degreasing with acetone, dried at room temperature and stored in moisture free desiccator before their use in corrosion studies.

2.2. Synthesis of imidazole derivatives

The NaOH solution of 25% (6.2 M) was added to a solution of imidazole (0.08 M) in CH_3CN and stirred for 10 min. To this solution, 1,4-bis(bromomethyl)-2,5-dimethoxybenzene (0.74 M) in acetonitrile was added at once and stirred at room temperature of 28 ± 1 °C for 48 h [30]. The reaction mixture was evaporated under reduced pressure and the residue obtained was extracted with CH_2Cl_2 (3 × 50 ml), washed with double distilled water (2 × 50 ml), brine (50 ml) and dried. The solvent was removed under vacuum and the residue was chromatographed using hexane/$CHCl_3$ (1:3) as eluent to give 1,4-bis(*N*-imidazolylmethyl)-2,5-dimethoxybenzene as a white solid.

In a similar synthetic way of BIDM, 1,3,5-tris(N-imidazolylmethyl)-2,4,6-trimethoxybenzene was synthesised as a white solid from imidazole (0.4 M) and 1,3,5-tris(bromomethyl)-2,4,6-trimethoxybenzene (17.14 M) using NaOH (6.4 M). The molecular structures of the as-synthesised imidazole derivatives are given in Fig. 1.

2.3. Characterization

The as-synthesized imidazole derivatives were purified and then characterized by ^1H and ^{13}C NMR spectra in $CDCl_3$ using deuterated dimethyl sulphoxide (DMSO) as internal standard on a JEOL GSX make with the frequency of 400 MHz NMR spectrometer. All the

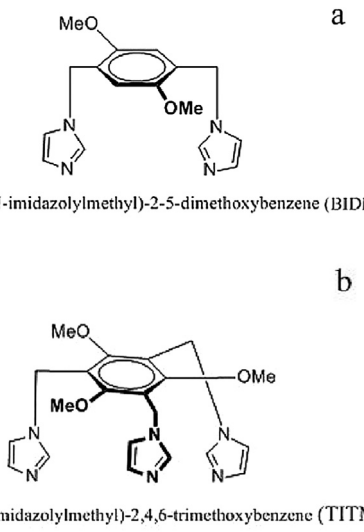

Fig. 1. Molecular structure of inhibitors (a) BIDM and (b) TITM.