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Quantum chemical calculations, molecular dynamics simulation and experimental studies of using some azo dyes as corrosion inhibitors for iron. Part 1: Mono-azo dye derivatives

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ABSTRACT

This study consists of two parts. In the first part, the inhibitive performance of six mono-azo dye (MAD_**1**–**6**) derivatives was investigated experimentally (gravimetric, thermometric, UV–visible spectrophotometric and electrochemical potentiostatic methods) and computationally against corrosion of Fe metal in 2 M HNO_3 and 2 M NaOH solutions. Density functional theory (DFT) calculations and molecular dynamics simulation (MDS) approach were performed. Quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap between E_{LUMO} and E_{HOMO} (ΔE), dipole moment (D), chemical hardness (η), softness (σ), electronegativity (χ), proton affinity, global electrophilicity (ω), global nucleophilicity (ε) and total energy (sum of electronic and zero-point energies) were calculated and discussed with the help of HF/SDD, HF/6-311 G, HF/6-31++G, B3LYP/SDD, B3LYP/6-311 G and B3LYP/6-31++G methods. Polarization measurements indicate that (MAD) compounds are of mixed-type inhibitor in acidic, act mainly as cathodic in alkaline solution. Kinetic model involving binding constant (K_b), active sites ($1/y$) and standard free energy values of adsorption (ΔG^o) were compared with the parameters of equilibrium constant (K_{ads}), lateral interaction (f) and (ΔG^o), that obtained from Frumkin adsorption isotherm model. Then, we calculated binding energies on Fe (110) surface of the inhibitors. The theoretical data obtained are in good agreement with the experimental inhibition efficiency results.

1. Introduction

Metals and alloys used in many engineering applications are susceptible to corrosion in aqueous media. Iron and its alloys, the most widely used among them, is also highly susceptible to corrosion, especially in acidic and alkaline media [1–5]. One of the best known methods for corrosion protection is the use of inhibitors [6,7]. Different types of organic compounds have been reported to act as inhibitors of corrosion [8–14]. Azo dyes as the most widely used as inhibitors class is controlled by its economic availability, its efficiency to inhibit the substrate material and its environmental side effects [15–19]; their application in various fields, such as the dyeing of textiles, and fibbers [20]. The presence of –N=N– group in azo dye molecules enhances their adsorption ability and corrosion inhibition efficiency. The planarity (π) and lone pair of electrons present on the N atoms are the important structural features that determine the adsorption of these molecules on to the metal surface [1]. The inhibition effect was also found to depend on some physicochemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density on donor atoms, and orbital character of donating electrons [21]. Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity [22] of potent inhibitors [23]. Thus, it has become a common practice to carry out quantum chemical calculations in corrosion inhibition studies. The predicted properties of reasonable accuracy can be obtained from density functional theory (DFT) calculations [24,25]. Some quantum chemical parameters, which influence the electronic interaction between surface atoms and inhibitors, are the energy of highest occupied molecular orbital (E_{HOMO}), the energy of lowest unoccupied molecular orbital (E_{LUMO}), the energy gap $E_{HOMO} - E_{LUMO}$ (ΔE) and dipole moment (D), chemical hardness

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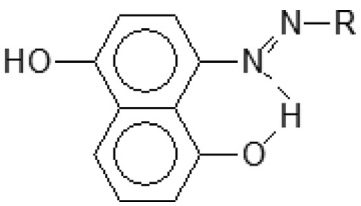
(η), softness (σ), electronegativity (χ), proton affinity, global electrophilicity (ω), global nucleophilicity (ε) and total energy (sum of electronic and zero-point energies). Previously, some work has been done in our laboratory on using mono– and bis–azo dye compounds as inhibitors on aluminum in HCl and NaOH solutions [26].

The aim of the present study was to investigate and compare the inhibition of corrosion of iron in 2.0 M HNO_3 and 2.0 M NaOH solutions by six synthesized mono-azo dye derivatives shown in Fig. 1 at 303 K. We have determined the inhibition efficiencies of these compounds using weight loss, thermometric, spectroscopy measurements and polarization curves method. Theoretical studies on electronic and molecular structures of substituted mono-azo dyes were carried out with the help of quantum chemical calculations and molecular dynamics simulations (MDS) approach to determine the most effective corrosion inhibitor among them.



R=
α-Naphthyl; the compound namely mono-α-naphthyl amine (MAD_**1**)
β- Naphthyl; the compound namely mono -β -naphthyl amine (MAD_**2**)
C_6H_4OMe-*p*; the compound namely mono -p-anisidine (MAD_**3**)
C_6H_4Me-*p*; the compound namely mono -p-toluidine (MAD_**4**)
C_6H_4Me-*o;* the compound namely mono -o-toluidine (MAD_**5**)
C_6H_4Me-*m*; the compound namely mono -m-toluidine (MAD_**6**)

2. Experimental details

2.1. Synthesis of the mono-azo dye compounds

The investigated mono-azo dye (MAD_**1**–**6**) derivatives were synthesized by diazotization of primary aromatic amines and coupling with the corresponding naphthol derivatives in the ratio 1:1. The compounds are purified and characterized by elemental analysis, IR, UV–visible spectroscopic investigation; mass spectroscopy and ^{1}Hnmr spectra spectroscopy techniques. The inhibitor solutions were prepared by dissolving the appropriate amount in 10 cm^3 Analar ethanol. The desired volume of the free inhibitor was added to the electrolyte solution. The ratio of ethanol was kept constant for each test. This stock solution was used for all experimental purposes. The concentration range of azo dye inhibitors employed was 5×10^{-7} M – 10^{-4} M at 303 K. The chemical structure and IUPAC name of synthesized azo dye compounds are given in Fig. 1. The corrosion tests were performed on iron specimens of following composition (wt. %): C=0.16, Mn=0.37, Si=0.05, S=0.015 and remainder Fe. Iron specimens of size $2.0\times2.0\times0.1$ and $10\times1\times0.1$ cm were used for weight loss and thermometric measurements, respectively. Solution of 2.0 M HNO_3 and 2.0 M NaOH were prepared by dilution of Analar analytical grade using double distilled water.

2.2. Measurements

2.2.1. Weight loss measurements

Weight loss experiments were done according to the standard methods as reported in literature [27]. The corrosion rates,

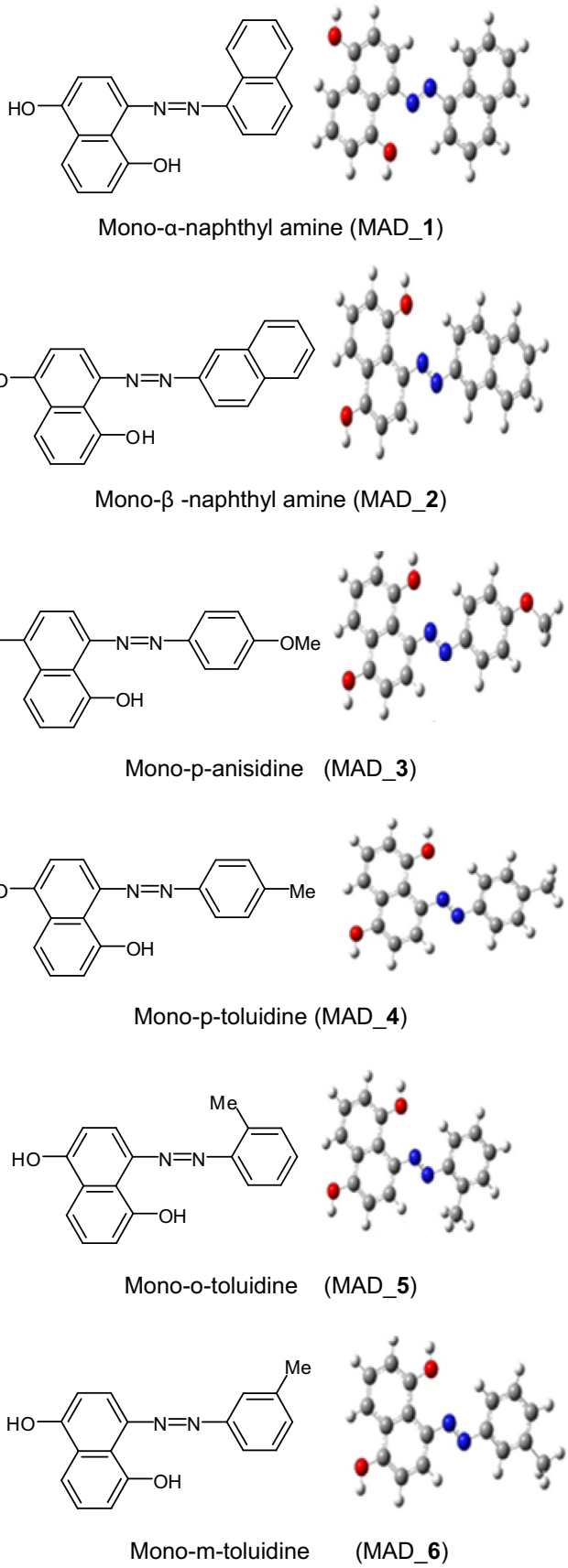


Fig. 1. Chemical molecular structures of synthesized mono-azo dye (MAD_**1-6**) derivatives.

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