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An investigation on the inhibitory action of benzazole derivatives as a consequence of sulfur atom induction

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ABSTRACT

The inhibitory action of three benzazole based molecules namely 2-methyl benzimidazole (2-MBI), 2-methyl benzothiazole (2-MBT) and 2-mercapto benzthiazole (2-SHBT) in 1 M HCl solution was studied by gravimetric analysis and electrochemical impedance spectroscopy (EIS). Results showed that the inhibitor adsorption on the iron surface was according to Langmuir adsorption isotherm for 2-MBI and 2-MBT and Flory Huggins Isotherm for 2-SHBT. Surface roughness obtained by Atomic Forced Microscopy (AFM) revealed that a good inhibitor decreases the surface roughness significantly which can be related to the formation of more integrated molecular film of inhibitor on steel surface. Based on contact angle (CA) measurements as the efficiency of the inhibitor molecules improve the hydrophobicity increases. These three molecules were chosen to see the effect of introducing sulfur atom into the structure the main effect of which would be on electronic parameters. To better understand this effect, the quantum chemical descriptors including: E_{HOMO}, E_{LUMO}, energy gap (ΔE), dipole moment (μ), hardness (η), softness (σ), electronegativity index (χ), fraction of electrons transferred (ΔN), that are most relevant to the potential action of a molecule as corrosion inhibitor, have been calculated in water and vacuum. Electronic parameters of these three inhibitors have been studied using DFT/B3LYP, and HF methods with 6-31G (d,p) basis set.

1. Introduction

Organic corrosion inhibitors play the main role in minimizing metallic corrosion in a variety of industrial processes such as cleaning pipeline and oil well acidification. Among different choices hydrochloric acid solutions are widely used spatially in petroleum fields where mild steel is one of the major construction materials that face this corrosive environment [1]. It is generally accepted that organic corrosion inhibitors form a thin layer on the surface of metal to protect it. As reported by several authors [2–10] the effectiveness of organic corrosion inhibitors is related to their chemical composition, molecular electronic structure, surface charge density and their affinity for the metal surface. Specific interactions between heteroatoms like oxygen, nitrogen, sulfur and phosphorus play an important role in inhibition due to the free electron pairs they possess.

Recently, theoretical prediction of the efficiency of corrosion inhibitors has become very popular [4–7], although the derived parameters are fundamentally different from experimentally measured quantities but unlike experimental measurements there is no statistical error in quantum chemical calculations. However there is inherent error, associated with the assumptions required to facilitate the calculations. In using quantum chemistry-based parameters with a series of related compounds, the computational error is considered to be approximately constant throughout the series [7].

The aim of this work is to achieve a better understanding on the effect of introducing sulfur atom into benzazole based inhibitor, in this context quantum chemical calculation was applied together with experimental methods such as weight loss, electrochemical impedance spectroscopy and Atomic Force Microscopy in order to characterize the actual behavior of the inhibitor molecule.

This work intends to study inhibitory action of 2-methylbenzimidazole, 2-methyl benzothiazole and 2-mercapto benzothiazole in hydrochloric acid solution using weight loss, EIS and AFM as experimental techniques to characterize the effect of presence of sulfur atom as a softer atom in inhibitor molecule, the results of which would be compared with DFT predictions.

Studying benzimidazole [2–5], and some derivatives of benzoxazole and benzthiazole [6,7] are reported in literature but considering the changes that sulfur atom introduction can cause

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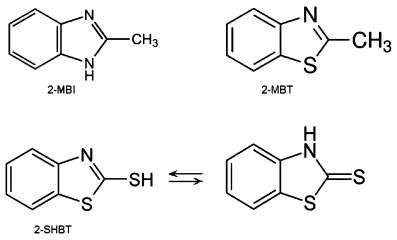

Fig. 1. The molecular structure of 2-MIB, 2-MBT and 2-SHBT.

Table 1
The elemental composition of the steel panels.

Elements	Fe	C	Si	Mn	P	S	Al
Wt%	99.01	0.19	0.34	0.32	0.05	0.05	0.04

in inhibitory action of the molecule is the unique feature of current work.

2. Experimental

2.1. Inhibitors

Three benzazole based compounds including 2-methyl benzimidazole (2-MBI); 2-methyl benzothiazole (2-MBT) and 2-mercapto benzthiazole (2-SHBT) were obtained from Merck and used without further purification. The molecular structures of these compounds are shown in Fig. 1. Labatory grade 37% HCl was purchased from Dr. Mojallali Co. to make 1 M HCl solution.

2.2. Weight loss measurements

The st-37 type steel panels (4 cm × 5 cm × 0.15 cm) were prepared from Foolad Mobarake Co. The elemental composition of the steel is presented in Table 1. Weight loss measurements were carried out in the glass vessel containing 250 mL of 1 M HCl solution without and with different concentrations of the inhibitor as illustrated in Table 2. The plates were polished with emery paper of grades 320–800, washed twice in deionized water, degreased with acetone and dried with compressed air flow. After immersion in acidic solution for 24 h at 293 K, the specimens were withdrawn and carefully washed with bi-distilled water and acetone, then dried and weighed. Triplicate experiments were performed in each case and the average value of the weight loss was calculated.

Table 2
The corrosion rate (CR) and inhibition efficiency (IE) obtained from weight loss measurements of mild steel in 1 M HCl containing various concentrations of 2-MBT.

Inhibitor	C (ppm)	CR (mpy)	IE%
2-MBI	Blank	245.94 ± 14	0
	50	223.20 ± 4.5	9.24
	100	206.89 ± 6.5	15.87
	200	180.48 ± 20	26.61
	400	145.98 ± 8.8	40.64
	800	90.43 ± 2	63.23
	1200	83.91 ± 0.5	65.88
	1400	71.76 ± 1	70.82
2-MBT	50	141.48 ± 1.5	42.47
	100	81.52 ± 10.1	66.85
	200	33.82 ± 1.7	86.24
	400	24.07 ± 2.3	90.21
2-SHBT	10	54.54 ± 3.8	77.82
	25	20.83 ± 1.8	91.53
	50	13.97 ± 2.1	94.32
	100	4.99 ± 0.5	97.97

2.3. Electrochemical measurements

The corrosion resistance of mounted samples with 1 cm^2 exposure area was also studied by an AUTOLAB PGSTAT12 type EIS. The perturbation and frequency range of the measurement was ±10 mV and 10 kHz–10 mHz respectively. The electrochemical measurements were carried out in a conventional three electrode system including platinum electrode (auxiliary electrode), KCl (3 N) Ag/AgCl electrode (reference electrode) and mounted sample (working electrode). The working electrodes were immersed in the test solution for 1 and 24 h to see the effect of immersion time on adsorption process.

2.4. Atomic forced microscopy (AFM)

The specimen of size 4.0 cm × 5.0 cm × 0.15 cm were polished with emery paper of grades 320–800, washed twice in deionized water (Millipore), degreased with acetone and dried with compressed air flow. After immersion in 1.0 M HCl without and with addition of inhibitor for 24 h, the specimen was cleaned with deionized water, dried with a cold air blaster, and then used for AFM examinations by means of an Ambios Technologies USPM.

2.5. Contact angle measurement

Contact angles of the metal surfaces were determined with a homemade instrument. Before fulfilling the contact angle Measurements, the metal coupons were immersed in 1 M HCl without and with the inhibitor in its ultimate concentration obtained from Weight loss measurements. Then the samples were removed from solution dried with a cold air blaster and kept in a desiccator. Contact angle of the surfaces was measured with Sessile Drop method by dropping 1 water drop to the metal surface from a syringe. The volume of the water that filled to the syringe was 4 μL. Three separate photos were taken from different parts of surfaces and contact angle values were measured for each drop. Measured contact angle values were obtained as the mean value of left and right contact angle.

2.6. Computational details

Electronic parameters of these three inhibitors have been studied using DFT/B3LYP, and HF methods with 6-31G (d,p) basis set. B3LYP, a version of the DFT method that uses Becke's three parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang and Parr (LYP) [5,11], was used in this paper to carry out quantum calculations using Spartan'08V1.2.0 program package. The theoretical parameters were calculated in vacuum, but to include the effect of 1 M HCl solution the parameters were also calculated in water.

Quantum chemical parameters including energy of the highest occupied molecular orbital (E_{HOMO}) and lowest unoccupied molecular orbital (E_{LUMO}), dipole moment and charge on possible active atoms on the azole molecules was calculated. According to DFT-Koopmans' theorem [12] the ionization potential, I, and electron affinity, A, can be approximated as the negative of E_{HOMO} and E_{LUMO} respectively (1) and (2):

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

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