Research Article

Gravimetric and Quantum Chemical Analysis of Brass Corrosion Inhibition by Inhibitors in Aqueous Medium

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Abstract

The corrosion behavior of brass in chloride solution is investigated in the presence of inhibitor namely 5-methyl benzotriazole (5MBTA), trisodium citrate (TSC) and sodium potassium tartrate (SPT). The inhibition efficiency of 5MBTA, TSC, SPT is evaluated from chemical and electrochemical techniques. Analysis of results revealed that of 5MBTA inhibits 71%. Quantum chemical methods are applied to determine the molecular structure, elucidating the electronic structure and reactivity towards the corrosion inhibitive property.

Keywords: Brass, Benzotriazole derivative, trisodium citrate, Sodium potassium tartrate, Quantum chemical study

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Introduction

Brass has been widely used as tubing material for condensers and heat exchangers in various cooling water system [1-2]. Brass materials are relatively noble. However 60-40 brass exhibited α- phase and is prone to corrosion attack. If the zinc content increases in the alloy, then the α-phase changes to β-phase which is more prone to corrosion attack. Due to the electrodissolution of metal in chloride solutions, there is a growing interest in inhibitors, for the application of copper or its alloys in marine environments. N-heterocyclic compounds have been widely used as corrosion inhibitors. Benzotriazole is a good anodic inhibitor for copper in acidic conditions14 and in chloride solutions [3].

One potential method to cost-effectively increase the corrosion inhibition efficiency is to employ the combination of inhibitors. The synergistic inhibition effect of combination of inhibitors has been studied by a number of authors [4-5]. The inhibition mechanism is generally explained that inhibitor molecules which are able to donate electrons, form coordinative bonds in the presence of vacant d-orbitals in copper [6]. Interaction with rings containing conjugated bonds, π-electrons, is also suggested [7]. Since, they are frequently responsible for good corrosion inhibition due to physically and/or chemically adsorption onto the surface [8].

Recently, it has been attempted to combine theoretical and practical approaches to investigate compounds with similar structure and find models that would enable to produce compounds acting as corrosion inhibitor. In this way, the quantum chemical methods enable the definition of a large number of molecular quantities characterizing the reactivity, shape, and binding properties of a complete molecule [9]. Highest occupied molecular orbital energy (EHOMO) and lowest unoccupied molecular orbital energy (ELUMO), also called frontier orbitals, determine the way the molecule interacts with other species [10]. Therefore, invaluable parameters acquired by quantum chemical method can help to understand the adsorption properties by considering the structure of every individual molecule.

The present work was devoted to the investigation of the corrosion behavior of 60-40 brass in NaCl medium. The effect of the addition of 5MBTA, TSC and SPT as inhibitor on the corrosion behavior of brass has been studied by the weight-loss method. Also, quantum chemical method has been used for identification of adsorption type and modeling corrosion inhibition by means of quantum chemical indices.

Experimental Details

The chemical composition (weight percent) of the of the brass plate used in these tests was 65.3% Cu, 34.44% Zn, 0.1385% Fe, 0.0635% Sn and the rest Pb, Mn, Ni, Cr, As, Co, Al and Sr as analyzed by optical emission spectrophotometer. The brass specimens were polished mechanically with SiC papers (120 -1200 grit), washed with double distilled water and degreased in acetone. The solutions were prepared from AR chemicals using DD water.

Weight Loss Method

Weight loss measurements were carried out using brass specimen of size 4 x 1 x 0.4 cm. The specimens were immersed in 100 ml of 3% NaCl solution with and without inhibitors at room temperature for 24 h.The Corrosion rate

CR and Inhibition efficiency IE were calculated using the following equation.

$$C = (534 \times W) / (D \times T \times A)$$

where A is the area, T the immersion time, W the weight loss and D the density of the specimen.

Quantum Chemical Analysis

Quantum chemical studies about corrosion inhibition efficiency have been successfully performed and the molecular properties were explained for different kinds of corrosion inhibitors [11, 12]. 5MBTA, TSC and SPTare focused to determine the theoretical inhibition efficiency. The molecular structures of the investigated compounds have been geometrically optimized by DFT method using 6-311G (d,p) basis sets with Gaussian-03 program.

Quantum chemical parameters such as the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), ionization potential, electron affinity, global hardness and softness have been calculated.

According to Koopman theorem, quantum chemical parameters such as the energy of highest occupied molecular orbital (E_{HOMO}), lowest unoccupied molecular orbital (LUMO), ionization potential(I), electron affinity(A), global hardness(η) and softness (σ) have been calculated using the following equation,

$$I = -E_{HOMO}$$
$$A = -E_{LUMO}$$
$$\eta = \frac{I-A}{2}$$

Correlations between the experimental inhibition efficiencies and quantum chemical parameters were investigated. The inhibition efficiencies of all inhibitors were compared with each other.

Results and Discussion

Weight loss method

Table 1 shows the inhibition efficiency (IE) and corrosion rate (CR) of brass by weight loss measurements at different inhibitor concentrations in 3% NaCl at room temperature. It is observed that the formulation consisting of 150 ppm of 5MBTA offers 71% IE and TSC shows the maximum inhibition efficiency of 43% at 400 ppm concentration and SPT shows the maximum inhibition efficiency of 29% at 400 ppm concentration.

Table 1 Corrosion rate and inhibition efficiency for various concentration of 5MBTA for the corrosion of brass in 3% NaCl

Conc. of 5MBTA (ppm)	IE (%)	Conc. of TSC (ppm)	IE (%)	Conc. Of SPT (ppm)	IE (%)
0	-	0	--	0	-
10	29	225	-14	200	11
50	43	330	-29	250	15
100	57	335	14	300	18
150	71	440	43	350	20
200	63	445	11	400	29
250	29	550	29	450	16
300	14	555	21	500	14

Quantum Chemical Analysis

Quantum chemical methods are applied to determine the molecular structure, elucidating the electronic structure and reactivity towards the corrosion inhibitive property. The selection of effective and appropriate inhibitors for the corrosion of brass has been widely carried out based on empirical approach [13]. Computational methods are used to understand and explain the functions of organic compounds in molecular terms. In the present investigation, quantum calculations are performed to study the relation between the molecular structure of 5MBTA, TSC, SPT.

The optimized molecular structure of the synthesized compound is shown in **Figure 1**. The quantum chemical indices containing E_{HOMO}, E_{LUMO} and dipole moment (μ), ionization potential, electron affinity, global hardness and

softness calculated by DFT method have been listed in **Table 2**. The energy difference between the HOMO and LUMO (ΔE) provides information about the overall reactivity of the molecule, the smaller the ΔE value is, the greater is the reactivity of the molecule [14]. From the Table 2, the ΔE value of the studied compounds shows that 5MBTA (ΔE = 5.1986 eV) is more reactive than TSC (ΔE = 5.6413eV), SPT (ΔE = 5.9492eV).

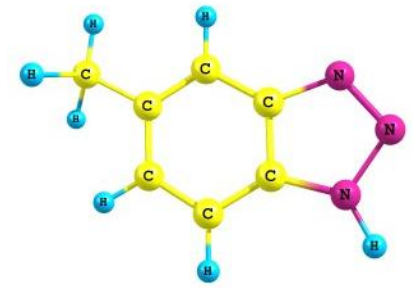
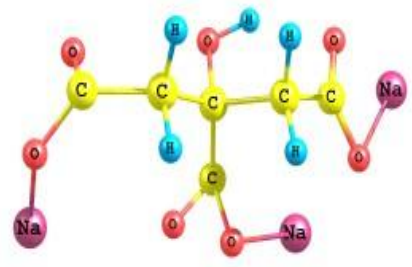
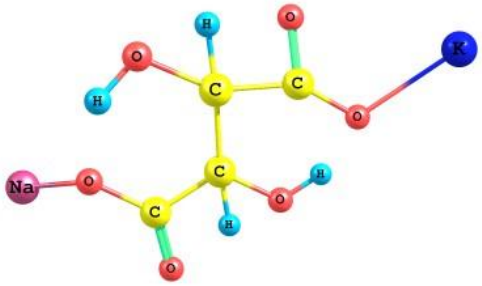
Name of the inhibitor	Optimized structure
5MBTA	
TSC	
SPT	

Figure1 Optimized structure of the studied inhibitor molecules obtained by B3LYP/6-311G level

Table 2 The calculated quantum chemical parameters for the selected inhibitors obtained using DFT at the B3LYP/6-311G (d,p) basis set

Quantum Chemical Parameters	5MBTA	TSC	SPT
Total energy (amu)	0.1910	0.0236	0.0716
Dipole moment(μ)	-2.5993	-2.8207	-2.9746
E_{HOMO} (eV)	-6.4375	-8.1595	-8.5531
E_{LUMO} (eV)	-1.2389	-2.5182	-2.6039
Energy gap (eV)	5.1986	5.6413	5.9492
Ionization potential (I)	6.4375	8.1595	8.5531
Electron affinity (A)	1.2389	2.5182	2.6039
Hardness (η)	2.5993	2.8207	2.9746
Softness (σ)	0.3847	0.3545	0.3362

The HOMO is the orbital that can act as an electron donor, since it is the outermost (highest energy) orbital containing electrons. The LUMO is the orbital that can act as the electron acceptor, since it is the innermost (lowest energy) orbital that has space to accept electrons. The HOMOs related to inhibitor (5MBTA) show that the benzene ring and N atoms have larger electron density. Thus, the benzene ring and N atoms can be suitable places for adsorption onto surface of brass, especially in the case of N because of their lone pair of electrons. Also, it can be claimed that bonding electrons of benzene rings create an electrostatic interaction. In other words the physisorption part in these inhibitors refers to existence of π-electrons in benzene rings of their molecular structure. In addition,

non-bonding electrons existing in N atoms make chemisorption or charge sharing or transferring from these organic compounds to brass surface.

Since molecular structure of these benzotriazole derivative (5MBTA) is in a manner that can simultaneously adsorb onto brass surface via N atoms, benzene ring and also the presence of electron donating methyl group in their structure which increases the electron density of the aromatic ring and makes the pi electrons more available to interact, they have ΔG values of physisorption.

Overall, 5MBTA molecule can be directly adsorbed at the surface on the basis of donor acceptor interactions between the π-electrons of benzene ring and N atoms, and the vacant d-orbitals of Cu and p-orbitals of Zn. It has been reported that excellent inhibition corrosion properties are usually obtained using organic compounds that not only offer electrons to unoccupied orbitals of the metal but also accept free electrons from the metal by using their anti-bond orbitals to form stable chelates [15]. Considering Table 2, it is understandable that present inhibitor molecule (5MBTA) can accept the d-orbital electrons of Cu and p-orbital electrons of Zn by LUMO on the benzene ring and N atoms. Consequently, this electron acceptance can help to form more stable bond between inhibitor molecule and brass surface atoms (Cu and Zn). In this study, 5MBTA with lower E_{LUMO} in comparison with TSC, SPT has higher efficiency and greater adsorption ability.

Other important properties to measure the molecular stability and reactivity are absolute hardness (η) and softness (σ). A hard molecule has a large energy gap and a soft molecule has a small energy gap. Soft molecules are more reactive than hard ones because they can easily offer electrons to an acceptor. For the simplest transfer of electrons, adsorption can occur at the part of the molecule, where the softness value is high [16].

In corrosion process the inhibitor acts as a Lewis base and the metal acts as a Lewis acid. Bulk metals are soft acids and thus soft base inhibitors are most effective for anodic corrosion of these metals [17]. In the present study, 5MBTA has higher (softness) σ value (0.3847) and lower (hardness) η value (2.5993). Normally, the inhibitor with the least value of global hardness η and highest value of global softness σ is expected to have the highest inhibition efficiency [18].

Therefore on interaction with the brass surface of studied inhibitors, 5MBTA would have the highest tendency to interact with the brass surface than TSC, SPT. Because 5MBTA has highest electron density centres due to the presence of hetro atom N, $-CH_3$ group substituent on benzene ring in comparison to other compounds conformed by values of smaller ΔE, higher σ, lower η.

The theoretical parameters have established the inhibitive effect of all inhibitors and supported the selected experimental results and conclusions in this study.

Quantum chemical parameters prove that the 5MBTA acts as a efficient inhibitor for corrosion of brass in industrial cooling water medium.

Conclusion

- 5MBTA inhibits the corrosion of brass in 3% NaCl solution and shows 71% IE at its optimum level of concentration (150 ppm) at room temperature for 24 hrs immersion at pH 7.
- Theoretical studies of quantum chemical analysis using DFT method show the inhibitive effect of 5MBTA, TSC, SPT on the basis of the number of adsorption sites, molecular size, mode of interaction and the physicochemical parameters.
- Quantum chemical parameters prove that the 5MBTA acts as a efficient inhibitor for corrosion of brass in 3% NaCl solution.
- The excellent inhibition efficiency of 5 methyl 1-H benzotriazole (5MBTA), enhanced synergistic influence of TSC with 5MBTA on corrosion inhibition of brass in 3% NaCl solution is strongly supported by the experimental, theoretical data.

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