Research Article

Theoretical and Experimental Investigations on Corrosion Control of 60Cu-40Zn Brass in Chloride Environment

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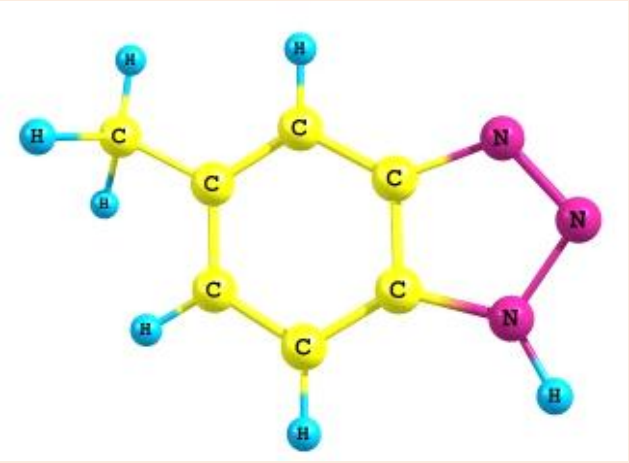
Abstract

The corrosion behavior of brass in chloride solution is investigated in the presence of inhibitor namely 5-methyl benzotriazole (5MBTA). The inhibition efficiency of 5MBTA is evaluated from chemical and electrochemical techniques. Experimental studies showed that 5MBTA reduces corrosion of brass in 3% NaCl solution. Polarization studies also revealed that the inhibitor act as mixed type for brass in chloride solution. The effect of temperature is studied in range between 303 & 333K and adsorption followed Langmuir isotherm. Quantum chemical study reveals that the benzene ring, and N atoms can be suitable sites for adsorption onto surface. Finally, an acceptable correlation between the theoretical and experimental inhibitor.



Optimized structure

Keywords: Brass, 5-methyl benzotriazole, Polarization, Adsorption isotherm, Quantum chemical study

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Introduction

Copper is metal that has a wide range of applications due to its good properties[1-3]. Brass has been widely used as tubing material for condensers and heat exchangers in various cooling water system[4-9] . 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. Among these,azoles are known as one of the best corrosion inhibitors for copper and its alloys in a wide range of environments [10–13] . Benzotriazole is a good anodic inhibitor for copper in acidic conditions[14] and in chloride solutions[15]. Frignani et al.[16] investigated the influence of alkyl chain on the protective effects of benzotriazole towards copper in acidic chloride solution and concluded that the inhibitors effectively control corrosion. (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 [17]. Interaction with rings containing conjugated bonds, π-electrons, is also suggested [18]. Since, they are frequently responsible for good corrosion inhibition due to physically and/or chemically adsorption onto the surface [19, 20-22].

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 [23]. 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 [24]. 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 as inhibitor on the corrosion behavior of brass has been studied by the weight-loss method and potentiodynamic polarization method. Also, quantum chemical method has been used for identification of adsorption type and modeling corrosion inhibition by means of quantum chemical indices.

2. Experimental details

2.1. Materials

The chemical composition (weight percent) of the of the brass plate used in these tests was 65% Cu, 35% 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[25].The solutions were prepared from AR chemicals using DD water. The structure of 5MBTA is given in Figure 1.

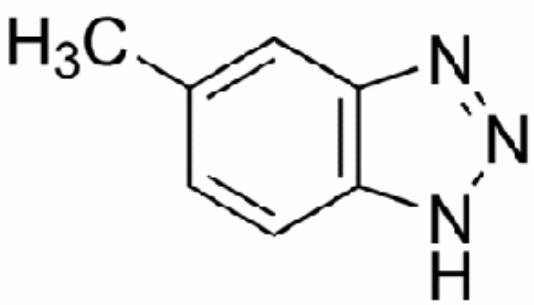

Figure 1 Structure of 5MBTA

2.2. Weight-loss method

Weight-loss measurements were carried out using brass specimen of size 4 cm x 1 cm 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 experiment was carried out at different temperature viz 303K,313K,323K,333K.

2.3. Potentiodynamic polarization study

The potentiodynamic polarization studies were carried out with brass strips having an exposed area of 1 cm^2. The cell assembly consisted of brass as working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as a reference electrode with a Luggin capillary bridge. Polarization studies were carried out using a potentiostat/galvanostat and the data obtained were analyzed.

The working electrode was immersed in a 3% NaCl solution and allowed to stabilize for 30 min[26]. Each electrode was immersed in a 3% NaCl solution in the presence and absence of optimum concentrations of the inhibitors to which a current of 1.5 mA cm^{-2} was applied for 15 min to reduce oxides. The cathodic and anodic polarization curves for brass specimen in the test solution with and without inhibitor were recorded at a sweep rate of 1 mV s^{-1}. The inhibition efficiencies of the compounds were determined from corrosion currents using the Tafel extrapolation method.

2.4. Quantum chemical study

Density functional theory (DFT) has been used to analyse the characteristics of the inhibitor/surface mechanism and to describe the structural nature of the inhibitor in the corrosion process[27,28]. It is considered to be a very useful technique to probe the inhibitor/surface interaction as well as to analyse the experimental data. This technique has been found to be successful in providing insights into the chemical reactivity and selectivity in terms of global parameters such as ionization potential, electron affinity, hardness, softness, etc.

The molecular structures of the both investigated compound have been geometrically optimized by DFT method using B3LYP level and 3-21G** basis set with Gaussian 98. Quantum chemical parameters such as the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and dipole moment (μ) have been calculated.

3. Results and discussion

3.1. 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 has been observed that the IE increases and CR decreases with increase in concentration of inhibitors and the optimum efficiency was 71% at 150 ppm concentration.The percentage of IE for different concentration of 5MBTA (ppm) increases in the following order 10 <50 <100 <150 and decreases at 200 ppm.

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

Conc. of 5MBTA (ppm)	Corrosion rate CR (mpy)	Surface Coverage (θ)	Inhibition efficiency IE (%)
0	0.395	-	-
10	0.282	0.286	29
50	0.225	0.429	43
100	0.169	0.571	57
150	**0.113**	**0.714**	**71**
200	0.146	0.571	63
250	0.282	0.286	29
300	0.338	0.143	14

3.2 Influence of temperature on IE of 5MBTA

The effect of temperature on the corrosion rate of brass in 3% NaCl solution and in presence of various concentration of 5MBTA was studied in the temperature range of 303K-333K using weight loss method. The calculated values of CR and IE are listed in Table 2. It is obvious that when the temperature increases, CR increases and IE of inhibitor decreases. This is due to the desorption of the adsorbed molecules of the inhibitor from the brass surface. This behaviour proves that the adsorption of inhibitor on brass surface occurs through physical adsorption[29] . Fig.2 indicates the variation of CR with temperature. It is found that in presence of 5MBTA the rate of brass dissolution increases with temperature, but at lower rate than in uninhibited solutions. Desorption is aided by increasing the reaction temperature[30]. At higher temperature, the decrease of IE is due to weak inter molecular vander waals forces of physical adsorption [31,32] on the brass surface and may also be due to the time lag between the process of adsorption and desorption becomes shorter as the temperature increases. As a result, corrosion rate increases consequently IE of inhibitor decreases[33].

Table 2 Corrosion rate and inhibition efficiency for various concentration of 5MBTA for the corrosion of brass in 3% NaCl obtained by weight loss method at various temperatures

Conc. of 5MBTA (ppm)	TEMPERATURE							
	303 K		313 K		323 K		333 K	
	CR (mpy)	IE%	CR (mpy)	IE%	CR (mpy)	IE%	CR (mpy)	IE%
0	0.395	-	5.410	-	7.214	-	8.566	-
10	0.282	29	4.058	25	5.861	19	7.664	11
50	0.225	43	3.607	33	5.410	25	7.213	16
100	0.169	57	2.705	50	4.058	44	5.410	37
150	**0.113**	**71**	**1.803**	**67**	**3.606**	**50**	**4.959**	**42**
200	0.146	63	2.954	45	4.058	44	5.860	32
250	0.282	29	4.058	25	5.861	19	7.213	16
300	0.338	14	4.959	8	6.763	6	8.116	5

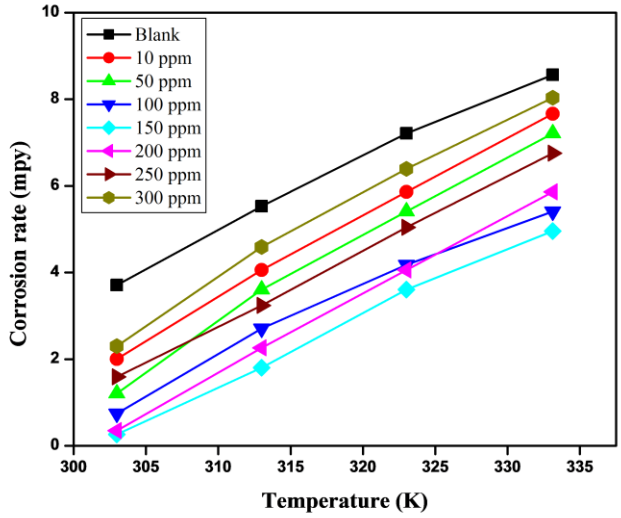

Figure 2 Plot of corrosion rate of brass with various temperatures

3.3 Thermodynamic activation Parameters

The kinetic thermodynamic model was a reliable tool to explain the mechanism of corrosion inhibition of inhibitor. The apparent activation[34] energy Ea^*, enthalpy change[35] of activation ΔH^* and entropy change[36] of activation ΔS^* for corrosion of brass in 3% NaCl solution in the absence and presence of 5MBTA were calculated from Arrhenius and Transistion state equations. The Arrhenius plot was obtained by log CR against 1/T is shown in Fig 3. A straight line was obtained and its slope is equal to $-Ea^*/2.303R$. The values of Ea^* for corrosion reaction with and without inhibitor were calculated and tabulated in Table 3. The results showed that the activation energy (Ea^*) for the corrosion of brass in the presence of 5MBTA is higher than blank. This can be attributed to the fact that higher values of Ea^* in the presence of inhibitor are generally consistent with physisorption, while lower values of blank solution suggests charge sharing or transfer from the organic inhibitor to the brass surface to form a coordinate covalent bonds .The increase in Ea^* can be attributed to an appreciable decrease in the adsorption of inhibitor on the brass surface with increase in temperature and a corresponding increase in corrosion rate occurs due to the availability of greater surface area exposed to corrosion .

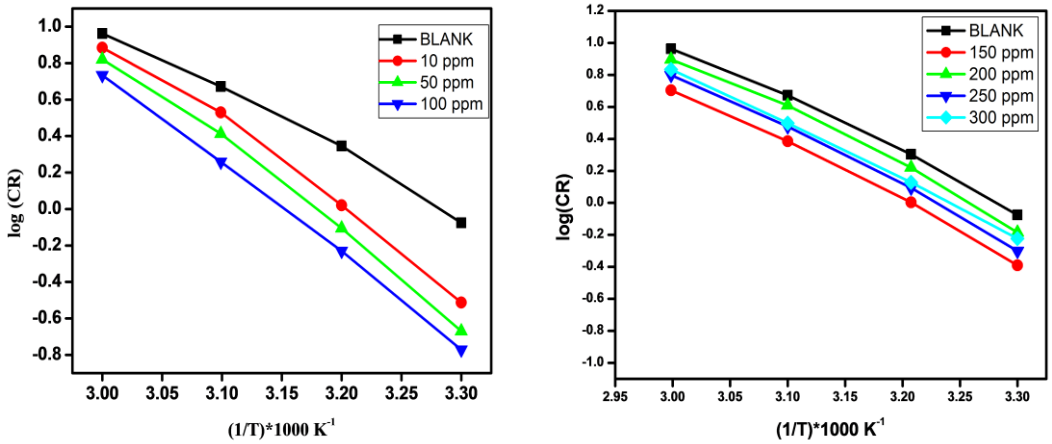

Figure 3 Arrhenius plot between log CR and 1/T for the inhibitor 5MBTA in 3% NaCl medium

Fig.4 showed plot of log (CR/T) against (1/T) for brass in 3% NaCl solution in the absence and presence of inhibitor are straight lines with slope equals to -ΔH* 2.303R and the intercept is logR/ Nh +ΔS*/ 2.303R. The obtained values of ΔH*and ΔS* are given in Table 3. Inspection of these results reveal that the activation enthalpy

ΔH* in inhibited solutions are higher than that of blank solution. The positive values of ΔH* reflect that the process of adsorption of the inhibitor on the brass surface is endothermic process. The values of ΔS* in the presence and absence of the inhibitor are less and negative. This implies that the activation complex is the rate determining step represents association rather than dissociation, indicating that a decrease in disorder takes place on going from reactants to the activated complex. The obtained results suggested that such types of inhibitor give a good inhibition at room temperature with considerable loss in IE at elevated temperature.

Table 3 Thermodynamic activation parameters of 5MBTA on brass in 3% NaCl

Conc. of 5MBTA (ppm)	Ea^* KJ/mol	ΔH^* KJ/mol	$-\Delta S^*$ KJ/mol
0	80.8595	76.2056	4.75
10	85.446	82.7157	23.24
50	88.8418	87.5024	37.32
100	89.8384	86.928	33.17
150	99.6032	97.459	64.18
200	94.2731	92.6722	51.26
250	83.4997	81.5668	19.53
300	86.6768	79.2692	13.64

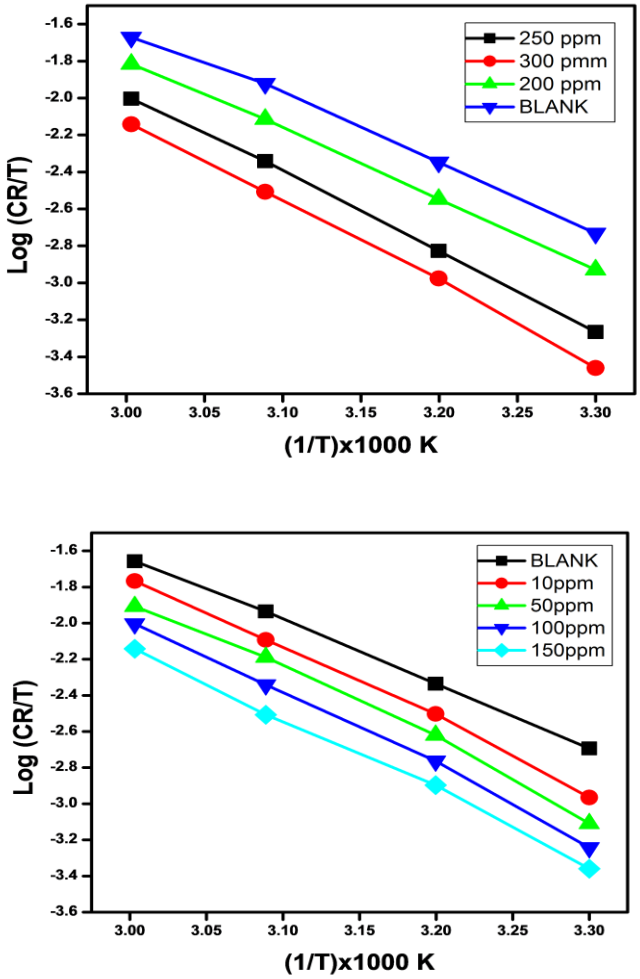

Figure 4 Transition state plot between log CR/T and 1/T for inhibitor 5MBTA in 3% NaCl

3.4 Adsorption isotherm

Organic molecules are used to inhibit corrosion as they are adsorbed on the metal – solution interface. The adsorption depends on the chemical structure of the inhibitor, chemical composition of solution, nature of metal surface, temperature and electrochemical potential at the metal – solution interface. The values of surface coverage (θ) corresponding to different concentrations of inhibitor are used to obtain the best adsorption isotherm. It has been found that data obeys only Langmuir adsorption isotherm.

By plotting values of (C/θ) vs C, linear plot was generated and is in shown Figure 5. The linear regressions are calculated, and the parameters are listed in Table 4. These results show that the linear correlation coefficient (r) is almost equal to 1, the slope is very close to 1, confirming that the experimental data fitted with the Langmuir adsorption isotherm. It indicates that adsorption of 5MBTA obeys the Langmuir adsorption isotherm and the best fit is at 303K.

Table 4 Parameters of the linear regression between log C/θ and logC

Linear correlation coefficient (r)	K	SLOPE
0.9557	0.5930	1.0398

Table 5 shows the value of ΔG at different temperatures[37]. The obtained value of -ΔG indicates the spontaneity and stability of adsorbed layer. From the table IV.7 , It is found that the ΔG_{ads} values are less than -40KJ/mol indicating that inhibitor molecules are stable and physically adsorbed (Physisorption) on the brass surface[38-40].

Table 5 Adsorption parameters of 5MBTA on brass in 3% NaCl at different temperature

Conc. of 5MBTA (ppm)	ΔG (KJ/mol)			
	303 K	313 K	323 K	333 K
10	-27.70	-27.11	-26.99	-25.95
50	-24.23	-23.97	-23.65	-22.79
100	-24.93	-24.57	-24.06	-24.01
150	-24.99	-24.72	-23.65	-23.50
200	-23.18	-23.04	-22.20	-21.45
250	-18.99	-18.73	-18.35	-18.33
300	-15.93	-14.86	-14.54	-14.48

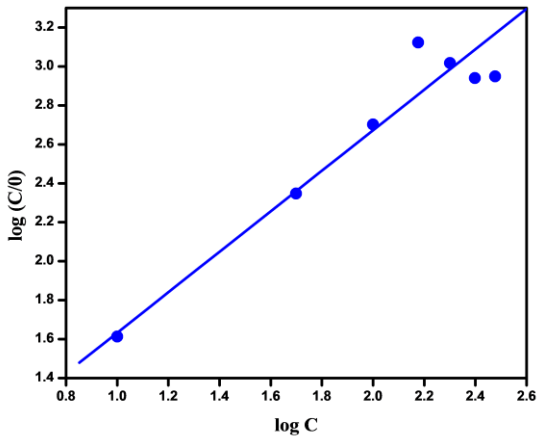

Figure 5 Langmuir plot

3.5 Analysis of the results of potentiostatic polarization study

Polarisation measurements are highly suitable for monitoring the progress[41].The cathodic and anodic polarization curves of brass in 3% NaCl solution with and without optimum concentration of 150 ppm of 5MBTA are shown in

Fig.6. It is evident that in the presence of inhibitor, the cathodic and anodic curves are shifted towards negative potential region and the shift is found dependent on the inhibitor. Electrochemical parameters namely, corrosion current density (Icorr), corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_a and b_c) are calculated from the tafel extrapolation of the polarization plot and also the CR[42-43] and IE values are calculated and reported in Table 6. The corrosion current density is decreased with inhibitor 5MBTA (2.42 µAcm$^{-2)}$ than with blank solution (7.34 µAcm^{-2}) as shown in Fig.5.9 and Table 5.8. The cathodic tafel slope and anodic tafel slope value of blank and inhibitor are found to differ from each other. For example, cathodic tafel slope of blank is 192 (mV/dec). However, its value is increased to 212.05 (mV/dec) for the inhibitor and anodic tafel slope b_a value is increased from 112 (mV/dec) to 242.13 (mV/dec). It indicates that the inhibitor 5MBTA controls both the reactions and behaves as a mixed type inhibitor. The mixed nature of inhibitor can be explained in terms of a change in E_{corr} values of inhibitor. If the displacement of E_{corr} value in presence of inhibitor is more than ±85 mV/SCE related to E_{corr} of blank, the inhibitor can be considered as cathodic and anodic[44]. If the change in E_{corr} is less than ± 85mV/SCE, the corrosion inhibitor may be considered as a mixed type inhibitor. The maximum displacement in the present study is 51.45 mV/SCE and indicates 5MBTA act as mixed type inhibitor. The corrosion rate in blank solution is found to be 3.65 mils year^{-1} and it is minimized by adding inhibitor to a lower value of 1.21 mils year^{-1} due to the adsorption of 5MBTA on the brass surface. The inhibition efficiency calculated from polarization study is 67% and is an excellent agreement with the value (71%) obtained from weight loss measurement. The slight variation in CR value is due to the long exposure of brass specimen in weight loss measurement but in electrochemical study is instantaneous. This behaviour (inhibition efficiency) of the inhibitor can be attributed to the presence of electron donar group N (aromatic cycle) in the molecular structure of 5MBTA. The presence of free electron pairs in the nitrogen atom and $(-CH_3)$ π electrons on the aromatic nucleus favours the adsorption of 5MBTA[45].

Table 6 Electrochemical parameters and inhibition efficiency of brass in 3%NaCl solution containing optimum concentration of 5MBTA

Conc. of 5MBTA (ppm)	I_{corr} (µAcm^2)	E_{corr} (mV/SCE)	b_a (mV/dec)	b_c (mV/dec)	Corrosion rate(mpy)	Inhibition Efficiency (%)
Blank	7.34	-232.29	112	192	3.65	-
150 (ppm)	2.42	-283.74	242.13	212.05	1.21	**67**

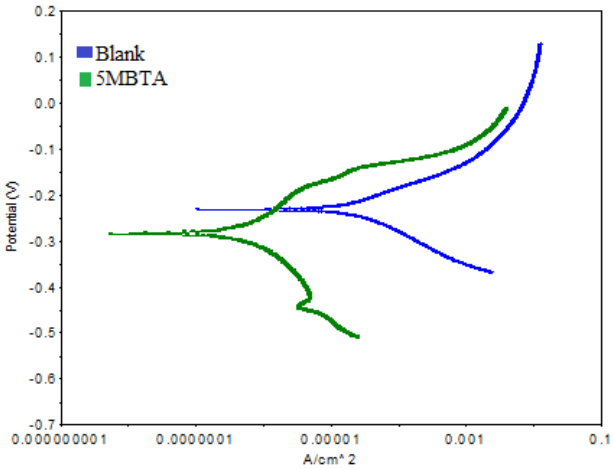

Figure 6 Polarization curves

3.6 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[27,28]. 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 about the molecular structure of 5MBTA. The design of the compound

5MBTA as a corrosion inhibitor is based on several factors. The molecule contains nitrogen atom as active centre. The optimized molecular structure of the synthesized compound is shown in Fig.7.

The quantum chemical indices containing EHOMO, E_{LUMO} and Dipole moment (μ), ionization potential, electron affinity, global hardness and softness calculated by DFT method have been listed in Table 7. 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. From the Table 7, the ΔE value of the studied compounds shows that 5MBTA (ΔE = 5.1986 eV) is more reactive. 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.

Considering Table 7, 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).

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. 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. In the present study, 5MBTA has σ value (0.3847) (softness) and η value (2.5993) (hardness). Therefore on interaction with the brass surface of studied inhibitor, 5MBTA would have the highest tendency to interact with the brass surface. Because 5MBTA has highest electron density centres due to the presence of hetro atom N, -CH_3 group substituent on benzene ring. The theoretical parameters have established the inhibitive effect of inhibitor and supported the selected experimental results and conclusions in this study. Quantum chemical parameters prove that the 5MBTA acts as an efficient inhibitor for corrosion of brass in industrial cooling water medium.

Table 7 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**
Total energy (amu)	0.1910
Dipole moment(μ)	-2.5993
E_{HOMO} (eV)	-6.4375
E_{LUMO} (eV)	-1.2389
Energy gap (eV)	5.1986

Ionization potential (I)	6.4375
Electron affinity (A)	1.2389
Hardness (η)	2.5993
Softness (σ)	0.3847

Optimized structure

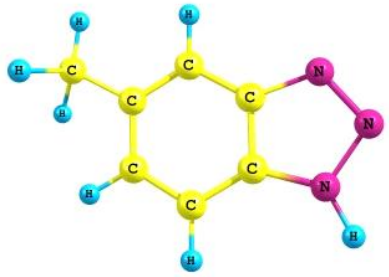

Figure 7 Optimized structure of 5MBTA

4. Conclusion

- Results of the weight loss method reveal that the formulation consisting of 150ppm of 5MBTA in 3% NaCl solution offers 71% IE on brass at 303K, for 24 hrs exposure time, at pH 7.
- Thermodynamical and kinetic parameters calculated by temperature study, graphical method and adsorption isotherms also strongly confirmed that 5MBTA act as an effective inhibitor in preventing brass corrosion under stationary as well as dynamic conditions.
- Polarization study reveals that this formulation acts as a mixed inhibitor but predominantly behaves as anodic type.
- Theoretical studies of quantum chemical analysis using DFT method show the inhibitive effect of 5MBTA 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.

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