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Full Length Research Paper

Inhibitive effects of 2-mercaptobenzimidazole (MBI) and 2-thiobenzylbenzimidazole (TBBI) on copper corrosion in 1 M nitric acid solution

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The inhibitive actions of 2-mercaptobenzimidazole (MBI) and 2-thiobenzylbenzimidazole (TBBI) on copper corrosion in 1M HNO_3 medium were studied, using weight loss method, at 25 to 65°C and concentrations of 5.10^{-5}M to 10^{-3}M. The results showed that the two compounds had fairly good inhibiting properties for copper corrosion in the medium, with efficiencies of 90.0% for TBBI and 87.7% for MBI at 25°C and concentration of 10^{-3}M. Modified Langmuir isotherm was found to provide an accurate description of the behavior of the two compounds. The thermodynamic functions of adsorption$\left(\Delta G^{\circ}_{ads}, Q_{ads}\right)$ and the activation energy (E_a) were calculated. Negative values of changes in free energies were obtained, indicating the spontaneity of the adsorption process. From thermodynamic adsorption and dissolution functions, both physisorption and chemisorption were proposed. Quantum chemical parameters such as highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE) and dipole moment (μ) were calculated for these compounds, using DFT/B3LYP/6-31G (d,p) method in order to discuss the correlation between theoretical data and experimental results. It was found that theoretical data support the experimental results.

Key words: Corrosion Inhibitor, inhibition efficiency, adsorption isotherm, free adsorption energy, adsorption heat, theoretical calculation, dipole moment.

INTRODUCTION

Corrosion is a phenomenon resulting from the physico-chemical interactions between a metal and its environment, driving to a deterioration of the metal's function, the surrounding environment and the technical system of which they make part: the resistance to corrosion is not an intrinsic property of a material; it essentially depends on the surrounding environment. Corrosion control depends on a discriminating choice of the materials and a rigorous control of the chemical composition of the environment.

Copper is widely used in various industrial operations; therefore the study of its corrosion inhibition is a subject of pronounced practical significance. This material is a relatively noble metal, requiring strong oxidants for its corrosion or dissolution; it is one of the most used metals in the industry because of its mechanical, thermal and electrical properties. It resists to the atmosphere and to numerous chemicals products. However, the acidic solutions (Kiss, 1988; Shaban, 1998; Jardy et al., 1992) used extensively in the industry for scouring or cleaning, for stimulation of oil wells or elimination of the localized deposits (tartar not distributed uniformly, rust, bacterial deposits…) and for the industrial synthesis provokes its dissolution. Copper is widely used in many applications such as manufacture of integrated circuits (Ho et al., 2001). The chemical dissolution and electrolytic plating are the main processes used in the fabrication of electronic devices. The most widely used corrosive solution contains nitric acid, so this medium induced a great deal of research on

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copper (Fiala et al., 2007). The deterioration of the metal caused by this medium makes inevitable the use of corrosion inhibitors (El Sayed et al., 2007).

Since one decade, the organic inhibitors are preferred to mineral ones because of the environment safety and also for their excellent inhibitory properties. However, not just any chemical compound can be used as corrosion inhibitor. There are some requirements that the compound must fulfill to do so. An organic compound must have some features that give it the ability to act as corrosion inhibitor. Among these, the number of adsorption active centers (Luo et al., 1998; Tadros et al., 1988), the charge density (Cao, 1996; Cumper et al., 1982), the mode of adsorption, the projected area (Hammouti et al., 1998) of the organic inhibitor, the molecular area and molecular weight (Ayers et al., 1963). Compounds with functional groups containing hetero-atoms (O, S N, P), which can donate lone pairs of electrons are found to be particularly useful as inhibitors for metal corrosion (Li et al., 2007), (Bouklah et al., 2006). Compounds with π-bonds also generally exhibit good inhibitive properties by providing electrons to interact with the metal surface (Benabdellah et al., 2007; Yildrim and Çetin, 2008; Fiala et al., 2007; Hasanov et al., 2007). Benzotriazole and benzimidazole are the most used inhibitors against the corrosion of copper (Scendo and Hepel 2008). Unfortunately, it is proven that benzotriazole and its derivatives are highly toxic compounds (Lisac et al., 2000); their use is limited therefore by the restrictions due to the protection of the environment (Cicileo et al., 1999).

In the present study, 2-mercaptobenzimidazole (MBI) and 2-thiobenzylbenzimidazole (TBBI) have been evaluated as corrosion inhibitors of copper in 1M HNO_3 solutions, using weight loss method. The molecules used in this work are not toxic and they have given good results in the inhibition of steel corrosion in 1M hydrochloric acidic environment (Aljourani et al., 2009).

The study was complemented by quantum chemical calculations based on DFT for the quantum calculation of molecular electronic structure. The calculation of quantum chemical parameters were carried out with Gaussian 03W suite of programs at density functional theory (DFT) level by B3LYP (Becke-3-lee-yang-Parr) method using 6-31G (d,p) basis set. The relation between the inhibition efficiency of the tested molecules and some quantum chemical parameters such as HOMO and LUMO energies, energy gap (ΔE) and the dipole moments (μ) were investigated. Quantum chemical calculations have proved to be a very powerful tool for studying corrosion inhibition mechanism (Bereket et al., 2003).

MATERIALS AND METHODS

Molecules structures

2- Mercaptobenzimidazole (MBI) is a compound, in powder, of whitish color; its molecular weight being M =150.2 g/mol whereas 2-thiobenzylbenzimidazole (TBBI) is rather of grayish color with molecular weight M = 240 g/mol. These organic compounds have been synthesized in the laboratory according to Van Allan method (Van Allan et al., 1963). Their molecular structures have been identified by RMN-^{1}H and ^{13}C spectroscopies and mass spectroscopy.

2-Thiobenzylbenzimidazole (TBBI)

^{1}H RMN (DMSOd-6) 4.57 (C$\underline{H}_2$, 2H, s), 7.10-7.16 (2H_{ar},m), 7.22-734 (3H_{ar},m), 7.44 (2H_{ar},m), 7.46-7.47(2H_{ar},m) ^{13}C NMR (50MHz, DMSOd-6) 35.12 ($\underline{C}H_2$), 114.08 (2C_{ar}) , 121.39 (2C_{ar}), 127.27 (C_{ar}), 128.44 (2C_{ar}), 128.80 (2C_{ar}), 137.64 (C_{ar}), 150 (C=N); SDM (E.I.) : M^{+1} = 241.

Analysis for $C_{14}H_{12}N_2S$: C(69.97%), H(5.03%), N(11.66%), S(13.34%).

2-Mercaptobenzimidazole (MBI)

: ^{1}H RMN (DMSOd-6): 7.10-7.16 (2H, m), 7.22-734 (2H, m); ^{13}C NMR (DMSOd-6): 114.08 (2C) 121.39 (2C), 128.44 (2C), 149.66(C=N); SDM (E.I.): M^{+1} = 151.
Analysis for $C_7H_6N_2S$: C(55.97%), H(4.03%), N(18.65%), S(21.35%).

Weight loss measurements

The weight loss measurements were performed with samples of copper in the form of rods measuring 10 mm in length and 2.2 mm in diameter that were cut from commercial pure copper (Cu 99.5 %).The corrosive solution of 1M HNO_3 was prepared by dilution of analytical grade 65% HNO_3 from MERCK with double distilled water. The samples were polished successively with metallographic emery papers of increasing fineness of up to 600 grits and further with 5, 1, 0.5 and 0.3 μm alumina slurries (Buehler), washed thoroughly with double distilled water, degreased and dried with acetone. The samples were then kept in a desiccator, weighed and immersed in the corrosive medium (50 mL of 1M HNO_3) with or without the tested inhibitors. A water thermostat SELECTA (FRIGITERM) controlled to ± 0.5 °C maintained the temperatures ranging from 25°C to 65°C. After 1 h, the specimens were removed, washed in 65% nitric acid for 5 s to remove the corrosion products, using bristle brush and rinsed with double distilled water, dried, kept in a desiccator and then reweighed. All tests were made in aerated solutions and were run triplicate to guarantee the reliability of the results. The corrosion rate (W) was calculated using the following equation:

$$w = \frac{m_1 - m_2}{S\,t} \tag{1}$$

Where m_1 and m_2 are respectively the weight (in g) before and after immersion in the test solution, S the total surface of the sample (in cm^2) and t the immersion time (in h).

The inhibition efficiency (%IE) was then calculated using the following equation:

$$\%\,IE = \frac{W_0 - W}{W_0} * 100 \tag{2}$$

w_0 and w are respectively the corrosion rates of copper in the absence and presence of the tested compounds.

RESULTS AND DISCUSSION

Corrosion rate and efficiency

The corrosion rate and the inhibition efficiency in presence of organic molecules depend on several factors such as the number of adsorption sites (N, S,O,P) and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface and the formation of metallic complexes (Fouda et al., 1986).

Figures 2 and 3 give the evolution of the corrosion rate of copper as a function of the concentration of TBBI or MBI for different temperatures.

From these figures, it can be seen that corrosion rate is concentration dependent: corrosion rate is reduced in presence of 2- thiométhylbenzimidazole (TBBI) and 2-mercaptobenzimidazole (MBI) compare to their absence (blank) in the nitric acid solution. We note that the addition of these molecules to nitric acid retards corrosion of copper in 1 M HNO_3 and that the extent of retardation is concentration and temperature dependent. Similar observations have been seen in the literature (Obot et al., 2009).

In Figures 4 and 5, it can be seen that for the same concentration, the efficiency increases when the temperature increases. These results can be explained by the adsorption of the studied compounds and indicate the formation of a protective film on the surface of the metal (Gopi et al., 2009). The increase in inhibition efficiency with inhibitor concentration indicates that the studied molecules are adsorbed on copper surface at higher concentration, leading to greater surface coverage. The inhibitory mechanism on copper dissolution is related to the chelating effect of Cu^{2+} ions close to copper surface. Indeed it is proven that copper is corroded to Cu^{2+} in HNO_3 solution and no oxide film is formed to protect the surface from corrosion (Pourbaix, 1975; Johnson and Leja, 1965). It is also known that the organic compounds can be adsorbed by the interactions between the lone pairs of electrons of nitrogen, sulfur or oxygen atoms with metal surface. These processes are facilitated by the presence of d vacant orbitals of low energy in the copper ions, as observed in transition group metals. Recently, it was found that the formation of donor-acceptor surface complexes between free electrons of an inhibitor and a vacant d orbital of a metal is responsible of the inhibition corrosion process (Zhang et al., 2009). The number of Cu^{2+} ions in proximity of copper increases with increasing temperature, leading to the formation of Cu^{2+}-inhibitor complexes protective film (increase in surface coverage) which create a physical barrier between Cu surface and the electrolyte, retarding the dissolution of the metal (Cicileo et al., 1999). The inhibition efficiency is then enhanced with increase in temperature (Figures 4 and 5).

Adsorption isotherm

The adsorption of an organic inhibitor on the surface of a corroding metal may be regarded as a substitution process between the organic compound in aqueous phase and water molecules adsorbed on the metal surface (Oguzie et al., 2007):

$$Org_{sol} + nH_2O_{ads} \leftrightarrow Org_{ads} + nH_2O_{sol}$$

The surface coverage (θ) was calculated as follows:

$$\theta = \frac{\% IE}{100} \qquad (3)$$

Basic information on the interaction between the inhibitor and the copper surface can be provided by the adsorption isotherm. It is necessary to determine empirically which adsorption isotherm fits best to the surface coverage data in order to use the corrosion rate measurements to calculate the thermodynamic parameters pertaining to inhibitor adsorption. In order to obtain the isotherm, linear relation between θ values and the inhibitor concentration C must be found. Attempts were made to fit the θ values to various isotherms including Langmuir, Temkin, Frumkin and Freundlich. The best fit was obtained with the Langmuir isotherm. Langmuir adsorption isotherm was found to be the best description of the adsorption behavior of the studied inhibitors; this adsorption isotherm is described by the following equation:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (4)$$

Where C is the inhibitor concentration, θ is the fraction of the surface covered and K the equilibrium constant of the adsorption process. Figure 6 shows the dependence of C/θ as a function of the concentration C for TBBI and MBI. The obtained plots are linear with correlation coefficients (R^2) almost equal to unity. It is also found that all the values of the slopes are very close to unity (R^2 = 0.999 and the slopes range from 0.962 to 1.008). The deviation of the slopes from unity is often interpreted as a sign that the adsorption species occupy more or less a typical adsorption site at the metal/solution interface (Hosseini et al., 2003). The divergence of the slopes from unity is attributable to interactions between adsorbate species on the metal surface as well as changes in the adsorption heat with increasing surface coverage. The Langmuir adsorption isotherm cannot be applied rigorously. A modified Langmuir adsorption isotherm (Ali et al., 2003) can be applied to this phenomenon which is given by the corrected equation:

$$\frac{C}{\theta} = \frac{n}{K} + nC \qquad (5)$$

The equilibrium constant of adsorption is related to the standard free energy of adsorption ΔG^0_{ads} by the following equation:

$$K = \frac{1}{55.5} . exp\left(-\frac{\Delta G^0_{ads}}{R.T}\right) \qquad (6)$$

Where R is universal gas constant, T the absolute temperature, 55.5 is the molar concentration of water in the solution in mol.L^{-1}. The adsorption equilibrium constant and the standard free energy of adsorption ΔG^0_{ads} (Tables 1 and 2) were calculated using Equations (5) and (6).

The negative values of ΔG^0_{ads} indicate a spontaneous adsorption process of TBBI and MBI on copper (Talati et al., 1983). It is generally accepted that for the values of ΔG^0_{ads} up to -20 kJ.mol^{-1}, the type of adsorption were regarded as physisorption; the inhibition acts due to the electrostatic interactions between the charged molecules and the charged metallic surfaces, while the values around -40 kJ.mol^{-1} or smaller were seen as chemisorption, which is due to the charge sharing or a transfer from the inhibitors molecules to the metal surface to form a covalent bond (Szlarska-Smialowaka, 1978), (Yurt et al., 2006). The values of ΔG^0_{ads} in our measurements range from -30 to -38 kJ.mol^{-1}: it is suggested that the adsorption of these molecules involves both types of interactions, chemisorption and physisorption.

Effect of temperature

To assess the effect of temperature on corrosion and corrosion inhibition processes, gravimetric experiments were performed at 10 K intervals in the temperature range 298 to 338 K with or without inhibitor. The relationship between the corrosion rate (W) of copper in the medium and the temperature (T) is expressed by the Arrhenius Equation:

$$W = k. exp\left(-\frac{E_a}{R.T}\right) \qquad (7)$$

Where E_a is the activation energy, k the preexponential factor and R the universal gas constant. The variation of logarithm of corrosion rate with reciprocal of absolute temperature is shown in Figure 7 for 1 M HNO_3 in absence and presence of inhibitor.

The slopes of these straight lines lead to the values of activation energies in respect of the inhibitors concentrations. An estimate of heat of adsorption was obtained from the trend of surface coverage with temperature as follows (Oguzie, 2004):

$$Q_{ads} = 2.303R\left[log\left(\frac{\theta_2}{1-\theta_2}\right) - log\left(\frac{\theta_1}{1-\theta_1}\right)\right]\left(\frac{T_1T_2}{T_2-T_1}\right) \qquad (8)$$

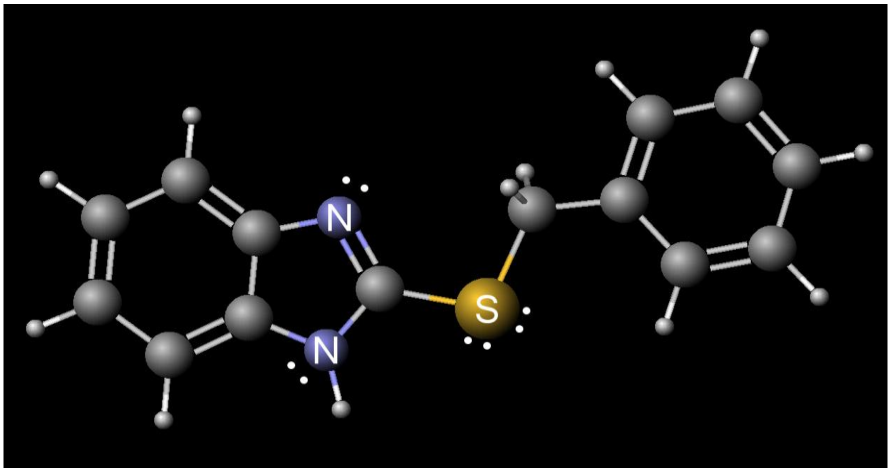
Where θ_1 and θ_2 are the degrees of the surface coverage at temperatures T_1 and T_2. The values of activation energies and heats of adsorption are listed in the Table 3.

Addition of TBBI and MBI is seen to reduce apparent activation energy for the corrosion reaction of copper in 1 M HNO_3. As temperature is raised, the inhibition efficiency %IE increased (Figure 8) and the activation energy E_a is lowered. The observed trend suggests likely specific interactions between the inhibitors and the metallic surface. Such a behavior has been attributed to a modification in the nature of adsorption, whereby the inhibitors are physically adsorbed at low temperature, whereas chemisorption is favored at high temperatures. Similar interpretations can be found in the literature (Popova et al., 2003).

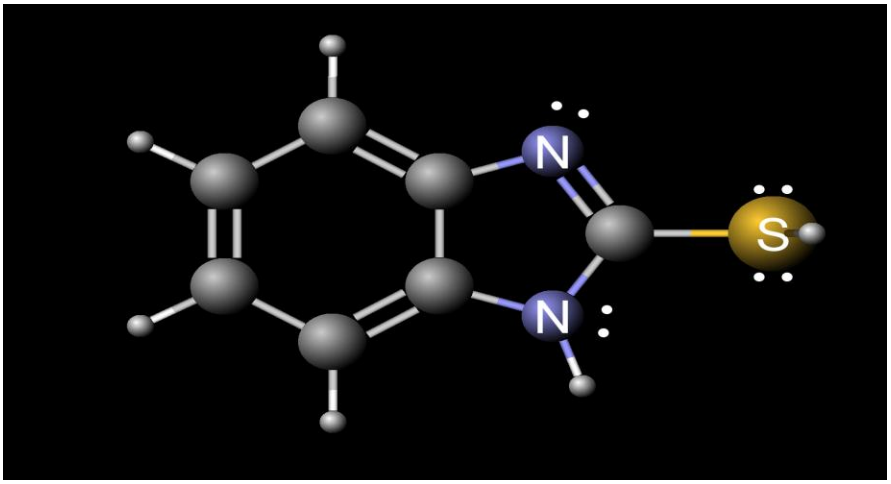
The positive Q_{ads} values obtained for TBBI and MBI indicate that the degree of surface coverage increases with rise in temperature and is consistent with the phenomenon of inhibitor chemical adsorption (Khaled, 2003). Increase in inhibition efficiency with increase in temperature may be attributed to a possible shift of the adsorption-desorption equilibrium towards adsorption of the inhibitors. Thus, as the temperature increases, the number of adsorbed molecules increases, leading to an increase in the inhibition efficiency.

Quantum chemical studies

Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity (Arslan et al., 2009). It has become a practice to carry out quantum chemical calculations in corrosion inhibition studies. So in order to obtain information about the electronic interactions of inhibitor molecules with the metal surface, the frontier orbital energies such as E_{HOMO}, E_{LUMO}, energy gap ($\Delta E = E_{LUMO}-E_{HOMO}$) and dipole moment (μ) are used to rationalize the reactivity of the inhibitor molecules. All the calculations have been performed by resorting to density functional theory (DFT) method level by B3LYP using the Gaussian 03 W suite of programs. The calculations were based on 6-31G (d, p) basis set. This basis set provided accurate geometry and electronic properties for a wide range of organic compounds (Henriquez-roman et al., 2005). To establish correlation between experimental data and structural and electronic characteristics of the studied compounds, the geometry of the molecules (Figure 1) were optimized by the density functional theory (DFT) method level with B3LYP exchange correlation functional, using 6-31G (d, p) basis set. We have determined quantum chemical parameters such as E_{LUMO}, E_{HOMO}, $\Delta E = E_{LUMO} - E_{HOMO}$, dipole moment μ, ionization potential ($I = -E_{HOMO}$) and electron affinity ($A = -E_{LUMO}$) of the studied molecules.



(a) **TBBI**



(b) MBI

Figure 1. Optimized chemical structures of a) 2-thiobenzylbenzimidazole and b) 2-mercaptobenzimidazole.

The obtained values of *I* and A were considered for the calculation of the electronegativity χ and the global hardness η in each of the tested molecule using the following relations (Pearson, 1989):

$$\chi = \frac{I+A}{2} \quad (9)$$

$$\eta = \frac{I-A}{2} \quad (10)$$

The fraction of electrons transferred from the inhibitor molecule to the metallic atom (ΔN) was calculated according to Pearson's formula:

$$\Delta N = \frac{\chi_{Cu}-\chi_{inh}}{2(\eta_{Cu}+\eta_{inh})} \quad (11)$$

The idea behind this is that in the reaction of two systems with different electronegativity as a metallic surface and an inhibitor molecule, the following mechanism will take place: the electron flow will happen from the molecule with the low electronegativity towards that of a higher value until the chemical potentials are the same. In order to calculate the fraction of electrons transferred, a theoretical value of electronegativity of bulk copper was used χ_{Cu} = 4.98 eV (Michaelson, 1977) and a global hardness $\eta_{Cu} = 0$ assuming that for a metallic bulk I = A (Dewar et al., 1985) because they are softer than the neutral metallic atoms. All the calculated parameters are listed in Table 4.

According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between frontier orbitals (HOMO and LUMO) of reacting species (Fukui, 1975). Thus, the treatment of the frontier molecular orbitals separately from the other orbitals is

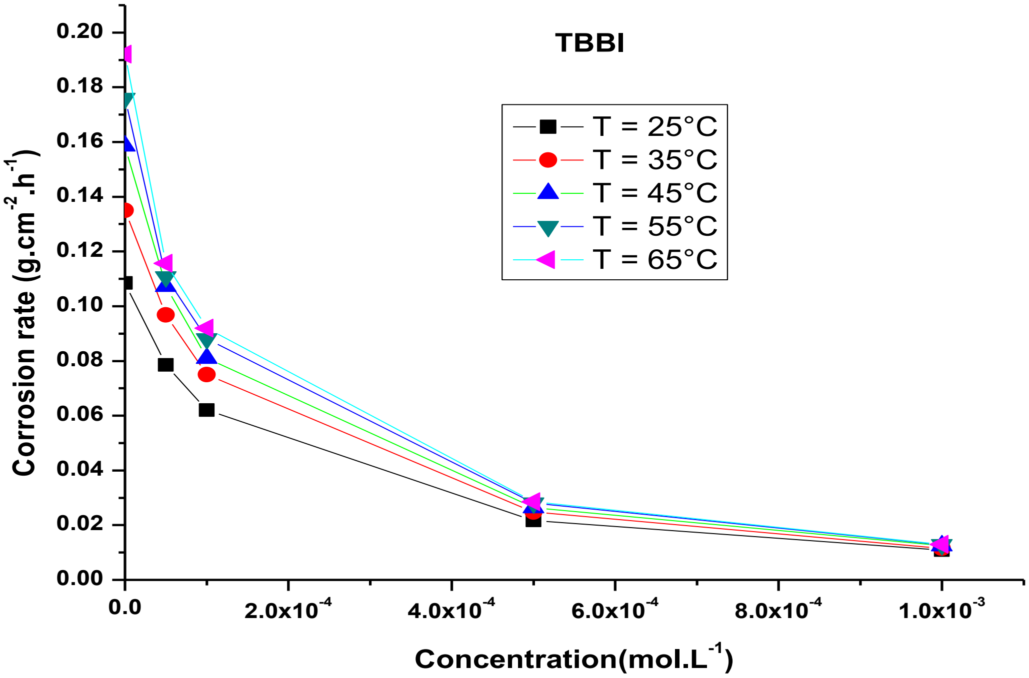


Figure 2. Variation of corrosion rate with inhibitor (TBBI) concentration at differen temperatures.

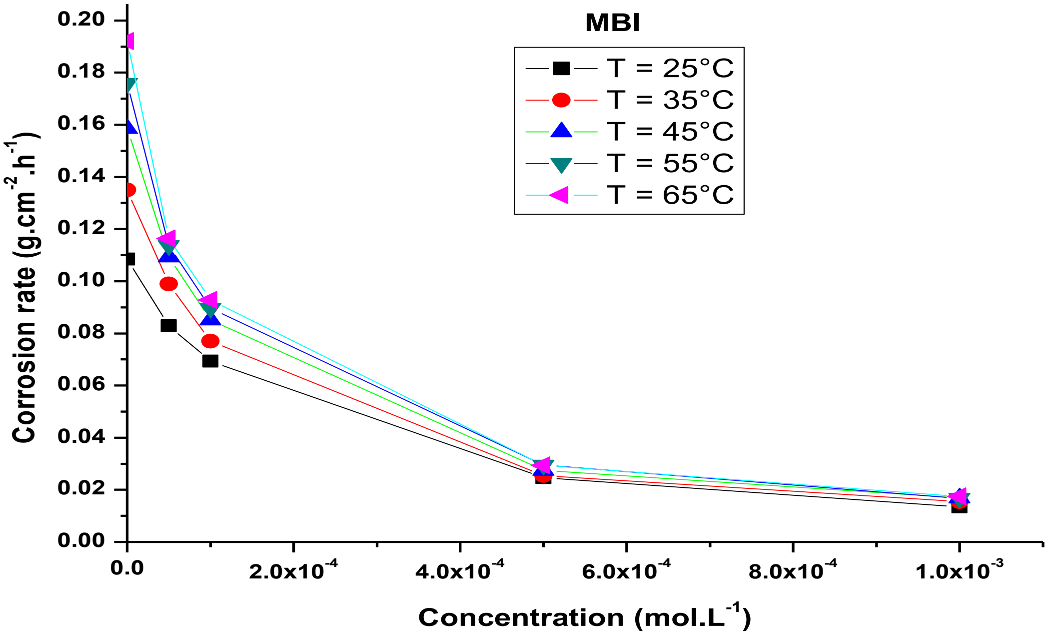


Figure 3. Variation of corrosion rate with inhibitor (MBI) concentration at different temperatures.

based on the general principles governing the nature of chemical reactions. HOMO is often associated with the electron donating ability of a molecule. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbital. Increasing values of the E_{HOMO} facilitate adsorption and therefore inhibition by influencing the transport process through the adsorbed layer (Gece, 2008).

E_{LUMO} indicates the ability of the molecules to accept electrons. The lower values of E_{LUMO}, the more probable it is that the molecule would accept electrons (Fukui, 1975). Low absolute values of the energy band gap (ΔE) gives good inhibition efficiencies, because the energy to

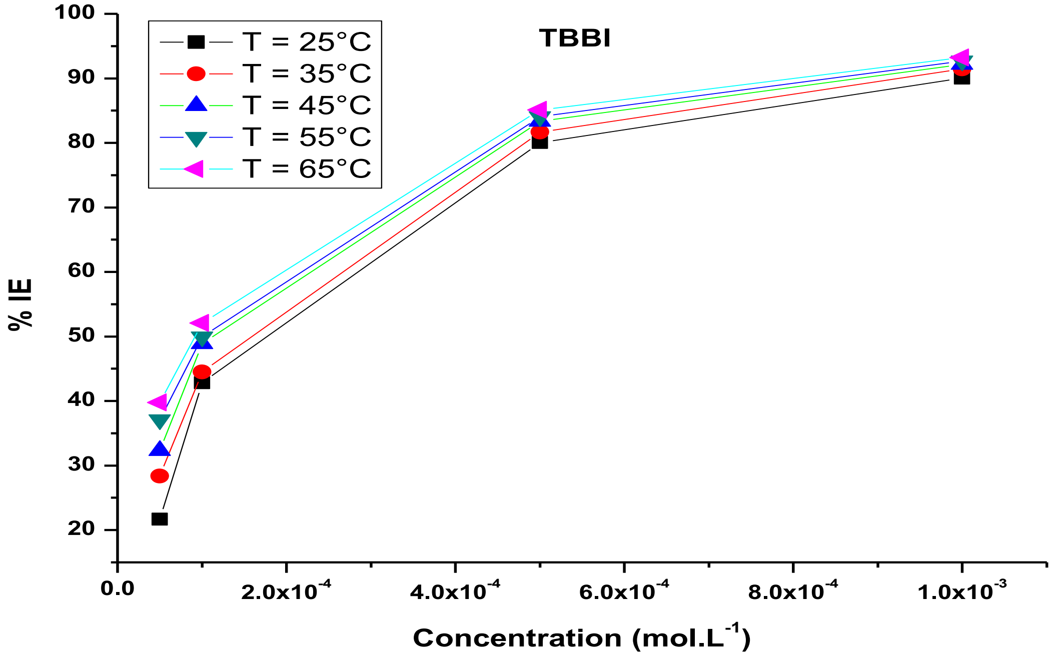


Figure 4. Variation of Inhibition efficiency with inhibitor (TBBI) concentration at different temperatures.

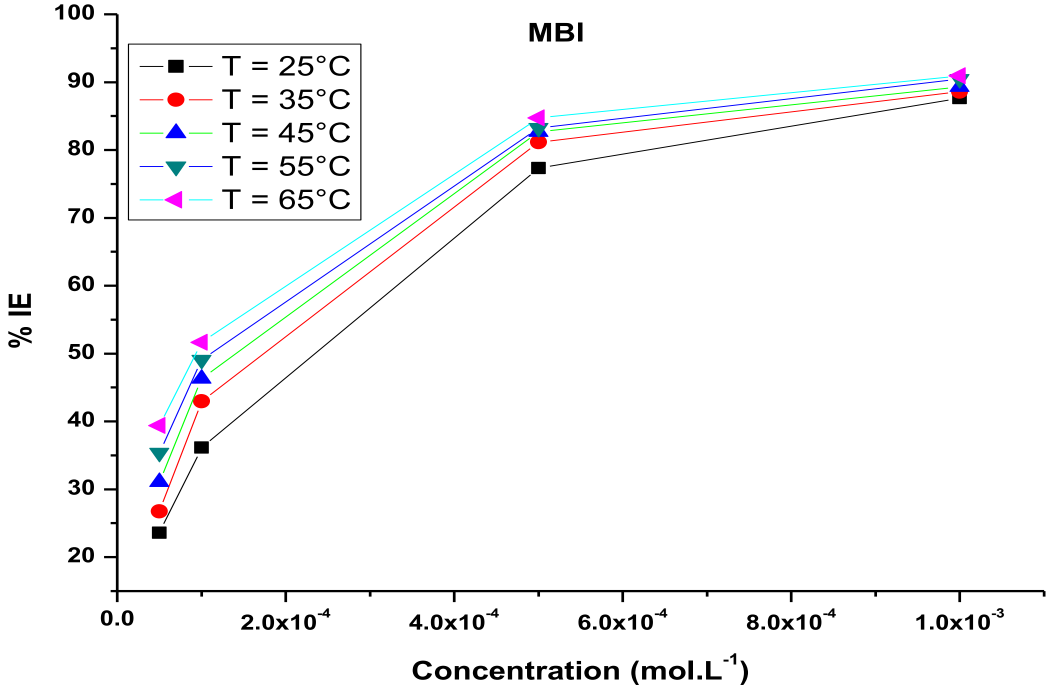


Figure 5. Variation of Inhibition efficiency with inhibitor (MBI) concentration at different temperatures.

remove an electron from the last occupied orbital will be low (Gece, 2008). In our case, TBBI has the highest HOMO energy (E_{HOMO} = -5.606 eV) value as compared to MBI. This leads to increase in adsorption on copper surface and accordingly increases its inhibition efficiency.

The quantum chemical calculations also confirms the lowest value of energy gap (ΔE = 5.122 eV) for TBBI when compared to MBI. This is in a good agreement with experimental observations suggesting that TBBI has the highest inhibition efficiency when compared to MBI.

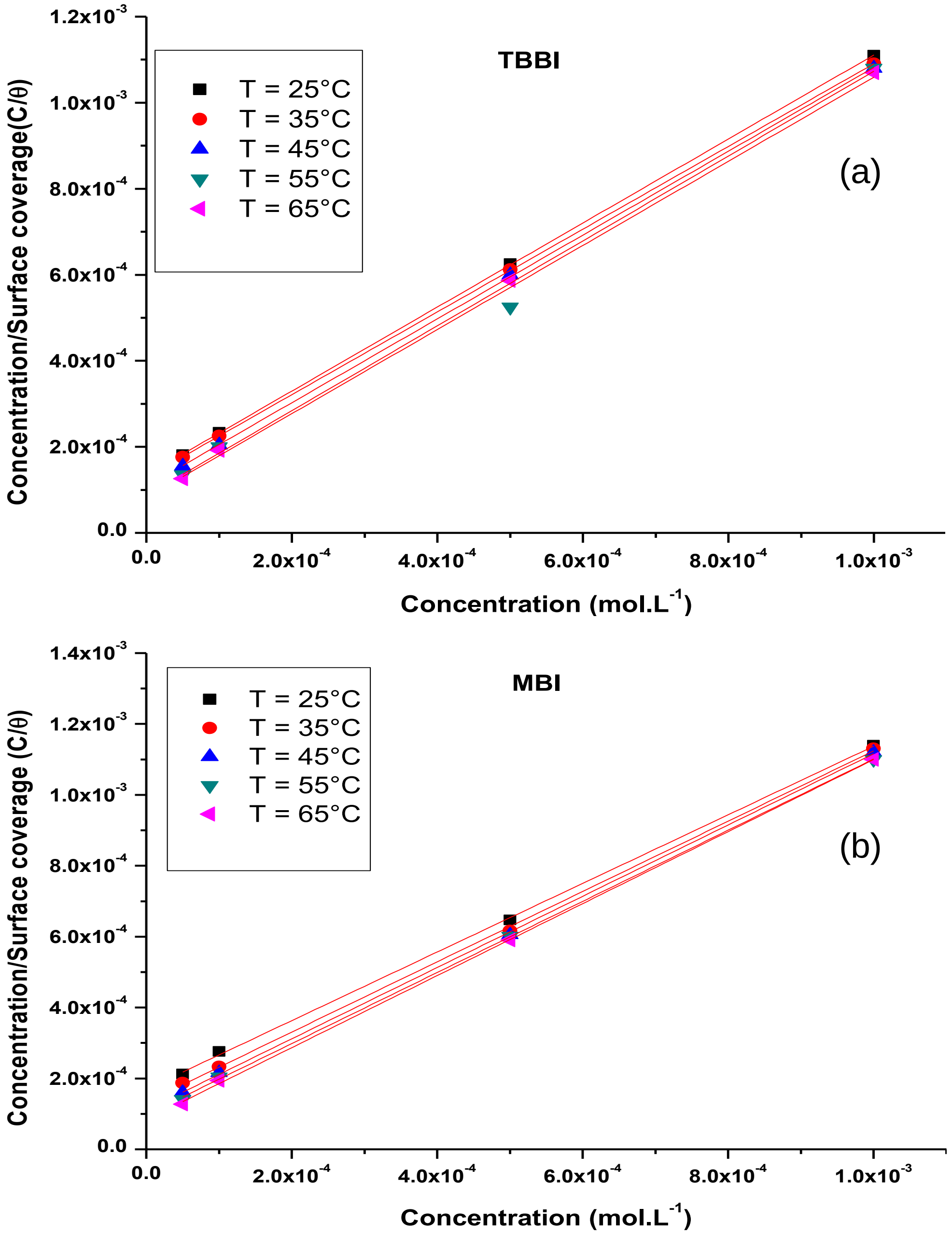


Figure 6. Langmuir adsorption plots for copper in 1 M HNO_3 containing various concentrations of inhibitor at different temperatures. (a) TBBI (b) MBI.

Table 1. Equilibrium constant K as a function of temperature.

Compound	**Equilibrium constant, K (L.mol^{-1})**							
	TBBI				**MBI**			
T(K) , C(M)	**5.10^{-5}**	**10^{-4}**	**5.10^{-4}**	**10^{-3}**	**5.10^{-5}**	**10^{-4}**	**5.10^{-4}**	**10^{-3}**
298	7655	7511	8025	9025	6166	5664	6813	7101
308	7916	8014	8907	10741	7305	7540	8617	7754
318	9559	9566	10020	11739	9010	8633	9546	8376
328	11785	9969	10560	12684	10952	9637	9927	9484
338	13193	10868	11450	13781	13000	10685	11078	10000

Table 2. Adsorption free energy $\Delta G°_{ads}$ as a function of temperature.

Compound	Adsorption free energy, ΔG°_{ads} $(kJ.mol^{-1})$							
	TBBI				MBI			
T(K) C(M)	5.10^{-5}	10^{-4}	5.10^{-4}	10^{-3}	5.10^{-5}	10^{-4}	5.10^{-4}	10^{-3}
298	-31.7	-32.1	-32.2	-32.5	-31.6	-31.4	-31.8	-31.9
308	-33.3	-33.3	-33.6	-34.1	-33.1	-33.2	-33.5	-33.2
318	-34.9	-34.9	-35.0	-35.4	-34.7	-34.6	-34.9	-34.5
328	-36.5	-36.4	-36.4	-36.7	-36.3	-36.0	-36.1	-36.0
338	-38.0	-37.4	-37.6	-38.1	-37.9	-37.4	-37.5	-37.2

Table 3. Calculated values of activation energy (E_a) and heat of adsorption (Q_{ads}) for copper dissolution in 1 M HNO_3 in the absence and presence of TBBI and MBI à 25 and 65°C.

System/Concentration	E_a $(kJ.mol^{-1})$	Q_{ads} $(kJ.mol^{-1})$
Blank	14.32	-
TBBI		
5.10^{-5} M	12.08	11.40
10^{-4} M	6.02	7.73
5.10^{-4} M	5.66	7.44
10^{-3} M	4.07	8.85
MBI		
5.10^{-5} M	10.42	15.60
10^{-4} M	7.76	13.29
5.10^{-4} M	6.13	10.17
10^{-3} M	5.63	7.16

According to these theoretical results and the experimentally found inhibition efficiencies (Table 4), it can be said that TBBI has more inclination to get adsorbed on the metal surface than MBI. Besides, the value of the gap provides a measure for the stability of the formed complex on the metal surface. The lower of ΔE, the higher stability is for the formed complex. Besides, it can be seen from Table 4 that the fraction of electrons transferred from the studied molecules to the metallic surface (ΔN) is in the same descent order as inhibition efficiencies.

The dipole moment (μ) is another indicator of the electronic distribution in a molecule and is one of the properties used to discuss and to rationalize the structure (Gao et al., 2007): low values of the dipole moment will favor the accumulation of inhibitor molecules on the metallic surface; besides it is an indication of the hydrophobic character of the molecules. In our case TBBI has the lower value of dipole moment compared to MBI, confirming that TBBI has more tendencies to get adsorbed on the metal surface. Similar results can be found in the literature (Khalil, 2003; Gao et al., 2007) even if survey of the literature reveals that several irregularities appeared in the case of the correlation of dipole moment with inhibitor efficiency (Bereket et al., 2002) .It can also be observed that TBBI has the highest values of molecular area and molecular mass what enhance its effective coverage onto the copper surface, leading to an increase in inhibition efficiency.

Conclusion

From the overall experimental results and discussion the following conclusions can be deduced:

(a) TBBI and MBI inhibit the corrosion of copper in 1M HNO_3.
(b) The inhibition efficiency increases with increase in inhibitors concentration and reaches a maximum value of 90.0 % for TBBI and 87.7 for MBI at 10^{-3}M and T = 298K.
(c) The inhibition efficiency increases with increase in temperature for TBBI and MBI.
(d) The adsorption of both inhibitors TBBI and MBI on copper surface obeys the Langmuir isotherm model.
(e) The thermodynamic and activation parameters obtained suggest physisorption at lower temperatures and chemisorption at higher temperatures for both

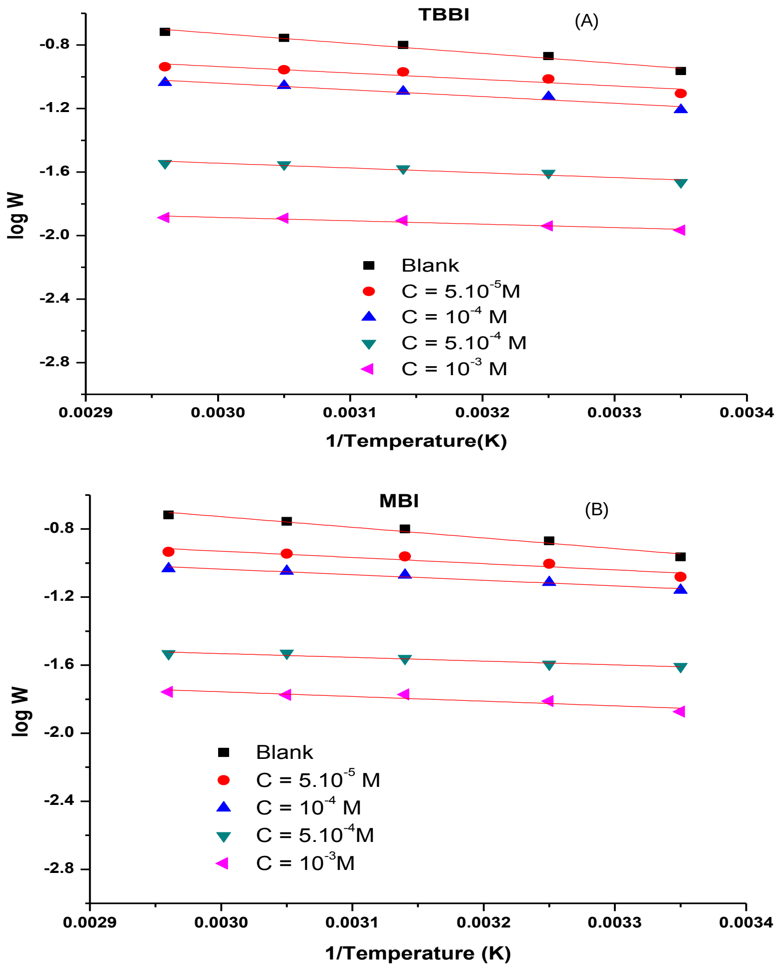


Figure 7. Arrhenius plots for copper corrosion in 1M HNO_3 without and with different inhibitor concentrations (a): TBBI (b): MBI.

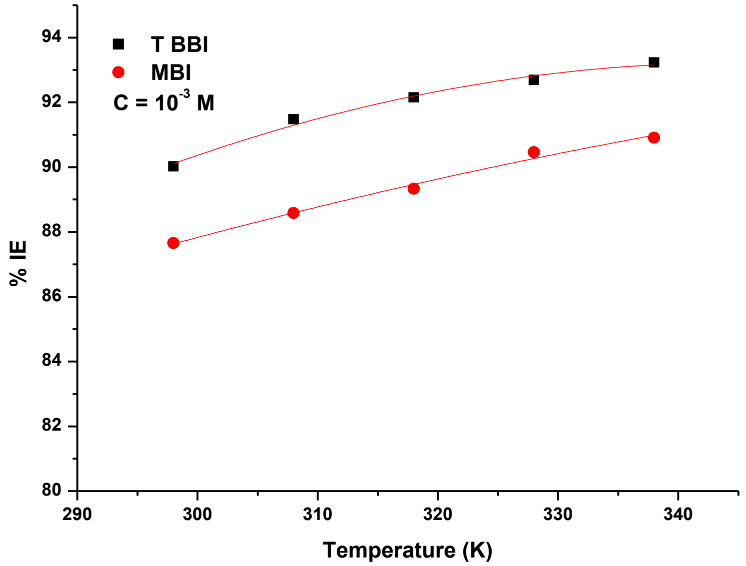


Figure 8. Inhibition efficiency of the studied inhibitors (TBBI and MBI) as a function of temperature.

Table 4. Quantum chemical parameters of the inhibitors from Gaussian 03W and % IE at C = 10^{-3}M and 25°C.

Compound	**DFT/B3LYP/6-31G (d,p)**						
	E_{HOMO} (eV)	**E_{LUMO} (eV)**	**ΔE (eV)**	**μ (Debye)**	**ΔN**	**Mwt (amu)**	**% IE**
TBBI	-5.606	-0.484	5.122	1.878	0.378	240.08	90.0
MBI	-6.033	-0.639	5.394	3.843	0.305	150.02	87.7

inhibitors.

(f) Quantum chemical calculations and the experimentally found inhibition efficiencies exhibit good correlation.

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