



Direct measurement of the adsorption kinetics of 2-Mercaptobenzothiazole on a microcrystalline copper surface

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ABSTRACT: The adsorption on copper of 2-Mercaptobenzothiazole (2-MBT), a heterocyclic compound member of the thiazole family, has been investigated at different concentrations (1×10^{-1} to 1×10^{-6} M) in water, employing the Electrochemical Quartz Crystal Microbalance (EQCM). The frequency response over time was obtained for each concentration, showing a defined exponential behavior at higher concentrations (1×10^{-1} , 1×10^{-2} and 1×10^{-3} M), which was fitted to the Langmuir adsorption isotherm with a good correlation coefficients ($R^2=0.91$ to 0.98). Surface coverage (θ) was calculated and found to be in the order of 0.50 to 0.01 for 2-MBT high concentrations. The free energy of adsorption was $\Delta G_{ads}=-5.59$ kJ mol⁻¹, corresponding to physisorption process, probably of electrostatic nature of the interaction between 2-MBT and copper surface in aqueous solution.

KEYWORDS: EQCM; Free energy of adsorption; Langmuir isotherm; 2-MBT

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RESUMEN: *Medición directa de la cinética de adsorción del 2-Mercaptobenzotiazol en una superficie micro cristalina de cobre.* En el presente trabajo se ha investigado la adsorción del 2-Mercaptobenzotiazol (2-MBT) en cobre, un compuesto heterocíclico miembro de la familia de los tiazoles, en solución acuosa a diferentes concentraciones (1×10^{-1} a 1×10^{-6} M), empleando la Balanza Electroquímica de Cristal de Cuarzo (BECC). Se midió y analizó el cambio de frecuencia con respecto al tiempo para cada concentración, mostrando un comportamiento exponencial definido en el rango de concentraciones altas (1×10^{-1} , 1×10^{-2} y 1×10^{-3} M), los cambios de frecuencia registrados se ajustaron usando la isoterma de adsorción de Langmuir obteniendo buenos coeficientes de correlación ($R^2=0,91$ a $0,98$). Se calculó también la fracción de superficie recubierta y se halló que se encuentra en el orden de 0,50 a 0,01 para las concentraciones altas de 2-MBT. La energía libre de adsorción calculada fue de $\Delta G_{ads}=-5,59$ kJ mol⁻¹, lo cual corresponde a un proceso de fisisorción.

PALABRAS CLAVE: BECC; Energía libre de adsorción; Isoterma de Langmuir; 2-MBT

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1. INTRODUCTION

Corrosion is a serious problem in many fields of industry, destroying the metal components in structures, electronic devices, vehicles, etc., as a consequence has a great impact on the economy of any

country. Thus, the protection of metals and alloys is of paramount importance for large industrial conglomerates and the search for effective means to prevent corrosion is a very active area.

Copper and its alloys are extensively used in industrial applications, ranging from construction

to electronics, this metal is present in almost every aspect of modern life (Davis, 2001). Copper is a relatively resistant metal in atmospheric neutral environments, in the absence of chlorides and SO₂, protected by the formed copper patina (Cu₂O). However, it is susceptible to corrosion in aggressive media, when the patina is converted to other corrosion products (Allam *et al.*, 2009). There are several methods to prevent metal corrosion and one of them is the use of inhibitors, organic or inorganic (Aballe *et al.*, 1997).

Organic inhibitors are compounds that, applied in very small concentrations, are capable of effectively reduce the corrosion rate. Many of them are heterocyclic compounds consisting of a π -system and/or containing O, N, or S heteroatoms (Schmitt, 1984; Quraishi and Jamal, 2001; Godínez *et al.*, 2003; Antonijevic and Petrovic, 2008; Khaled *et al.*, 2009; Behpour and Mohammadi, 2012; Pan *et al.*, 2013; Finšgar and Merl, 2014; Winkler *et al.*, 2014; Jakeria *et al.*, 2015). Among these compounds those of the azole group, containing nitrogen and/or sulphur, are considered as effective corrosion inhibitors for copper (Marconato *et al.*, 1998; Subramanian and Lakshminarayanan, 2002; Finšgar and Merl, 2014; Winkler *et al.*, 2014). Despite the fact that organic inhibitors have been extensively investigated in the last decades, their inhibition mechanism is usually unknown (Trabanelli and Carassiti, 1970; Chadwick and Hashemi, 1979; Zhang *et al.*, 2007; Morales-Gil *et al.*, 2014). It is generally accepted that inhibition is achieved by the formation of a protective film formed by adsorbed inhibitor molecules on the metal surface (Marconato *et al.*, 1998; Subramanian and Lakshminarayanan, 2002; Godínez *et al.*, 2003; Solmaz *et al.*, 2011; Kazansky *et al.*, 2012), which acts as a barrier between the aggressive media and the metal surface.

However, the kinetics of the formation process of this protective film remains unresolved. There are several techniques that can be used to study the adsorption process of organic molecules on metal substrates.

The most notable techniques are: measurement of mass change, using the electrochemical quartz crystal micro-balance (EQCM), measurement of contact angle, ellipsometry, reflectance absorption infrared spectroscopy (RA-IRS), surface plasmon resonance (SPR), electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM) (Subramanian and Lakshminarayanan, 2000).

The EQCM is a valuable tool that enables the acquisition of relevant data about the adsorption of chemical species (molecules or ions) on metallic substrates in the microscale and characterization of their adsorption kinetics (Eickes *et al.*, 2000; Telegdi *et al.*, 2000). It consists of a quartz resonator, sandwiched between two metal electrodes, these electrodes produce an oscillating electric field, causing

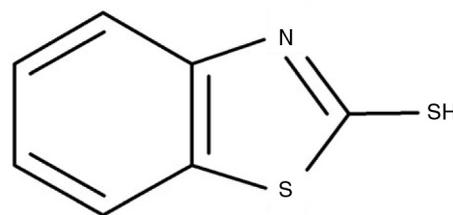


FIGURE 1. Schematic molecular structure of 2-MBT.

vibrational motion of the crystal at its fundamental frequency. The frequency is sensitive to the mass change of the resonator and when adsorption or desorption of mass occurs, a frequency shift is detected. Thus, adsorption will be registered as a frequency decrease, while desorption will produce a frequency increase.

The aim of this work is to enlarge the information about the adsorption of 2-Mercaptobenzothiazole (2-MBT, C₇H₅NS₂) see Fig. 1, a member of the azole's group, used as corrosion inhibitor for copper (Winkler *et al.*, 2014). The research was carried out employing the EQCM to obtain the frequency response over time, the adsorption isotherm, the fraction of surface coverage and the free energy of 2-MBT adsorption.

2. MATERIALS AND METHODS

Commercially available reactive grade (96%) Aldrich 2-Mercaptobenzothiazole, was used without further purification to prepare solutions with distilled water. The concentration range of 2-MBT was 1×10^{-6} to 1×10^{-1} M (pH=6.5).

The EQCM working electrodes are manufactured by Gamry Instruments and they consist of AT-cut quartz crystals coated with Cu, having an active area of 0.205 cm² and a sensitivity factor C_f of 226 Hz cm² μ g⁻¹, having a fundamental frequency of 10 MHz. All experiments were carried out in a Gamry Teflon Cell, specifically designed to be used with the EQCM working electrodes.

2.1. Frequency response over time

During 2-MBT adsorption process, conducted at 22 °C, EQCM 10M Gamry frequency monitor was used to record the frequency response during 3600 seconds, inside a Gamry Vista Shield Faraday Cage.

2.2. Adsorption isotherm

Frequency variations (Δf) detected by the EQCM are due to several contributions:

$$\Delta f = \Delta f_d + \Delta f_m + \Delta f_a + \Delta f_x \quad (1)$$

where Δf_d is the portion of the frequency shift related to viscous damping; Δf_m is caused by adsorbed mass; Δf_a is surface stress and Δf_x is caused by energy dissipation.

As can be seen the frequency shift (Eq. 1) is the result of a very complex process and it does not depend of only the mass change. Therefore, obtaining surface coverage information from frequency variation data is at least problematic. However, the time dependence of this frequency response is the result of the formation of an adsorbed monolayer, therefore the time domain measurements are sensitive to adsorption kinetics of the monolayer and thus, surface coverage information can be extracted from frequency response over time data (Karpovich and Blanchard, 1994). The obtained frequency shift data were fitted to the Langmuir isotherm (Langmuir, 1918; Karpovich and Blanchard, 1994; Subramanian and Lakshminarayanan, 2000; Marczewski, 2010; Haerifar and Azizian, 2013):

$$\theta(t-t_0) = K' [1 - e^{-(k_m)(t-t_0)}] \tag{2}$$

where $K' = C / [C + (kd)(ka^{-1})]^{-1}$; θ is the surface coverage; t is time; t_0 is the diffusion time and k_m is the rate constant of adsorption and it is related to the adsorption and desorption constants by the following relation:

$$k_m = k_a C + k_d \tag{3}$$

being k_a the adsorption constant, k_d the desorption constant and C the inhibitor concentration. A linear fit of k_m vs C gives k_a as the slope of the line and k_d as the intercept.

2.3. Fraction of surface coverage and free energy of adsorption

Surface coverage (θ) was calculated using the following equation:

$$\Theta = C / [C + K_{eq}^{-1}] \mid K_{eq} = (k_a)(k_d)^{-1} \tag{4}$$

where C is the inhibitor concentration and K_{eq} is the equilibrium constant (Karpovich and Blanchard, 1994). The free energy of adsorption ΔG_{ads} was found directly from equilibrium constant data, using the thermodynamic relation (Karpovich and Blanchard, 1994):

$$\Delta G_{ads} = -RT \ln K_{eq} \tag{5}$$

where R is the ideal gas constant and T is temperature.

3. RESULTS AND DISCUSSIONS

3.1. Frequency response over time

The frequency response for the adsorption of 2-MBT on copper is shown in Figs. 2–7. The curves were obtained inverting the Y-axis ($-\Delta f$ vs t). The

observed frequency shift follows a well-defined exponential law, when 2-MBT concentration was in the range of 1×10^{-1} to 1×10^{-2} M (Fig. 2 and Fig. 3).

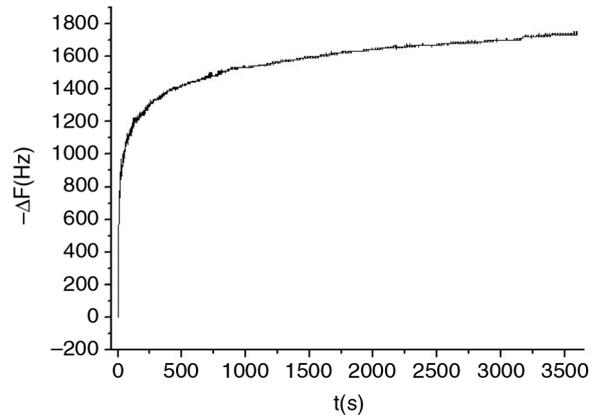


FIGURE 2. Frequency response over time of 1×10^{-1} M 2-MBT on copper.

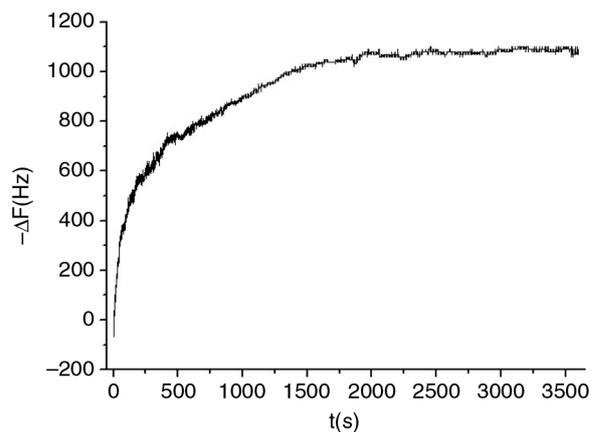


FIGURE 3. Frequency response over time of 1×10^{-2} M 2-MBT on copper.

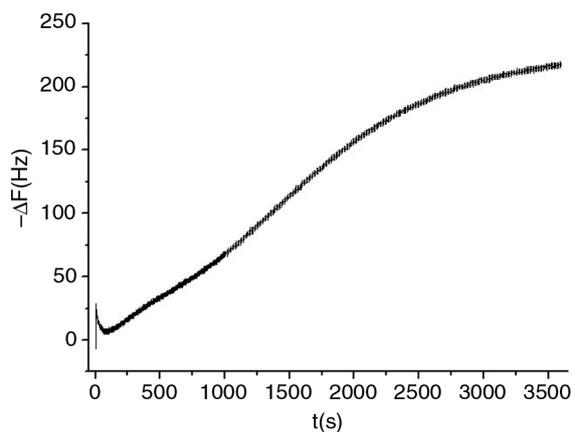


FIGURE 4. Frequency response over time of 1×10^{-3} M 2-MBT on copper.

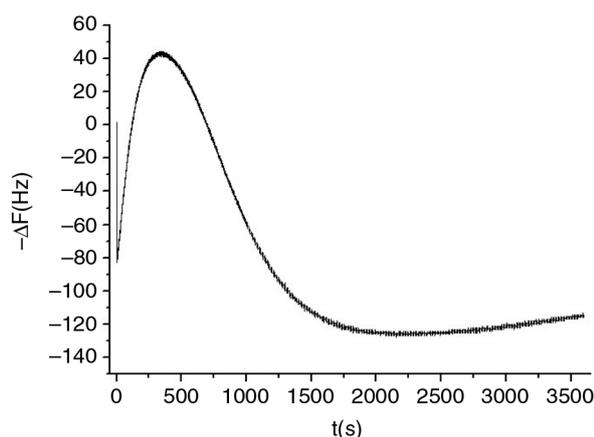


FIGURE 5. Frequency response over time of 1×10^{-4} M 2-MBT on copper.

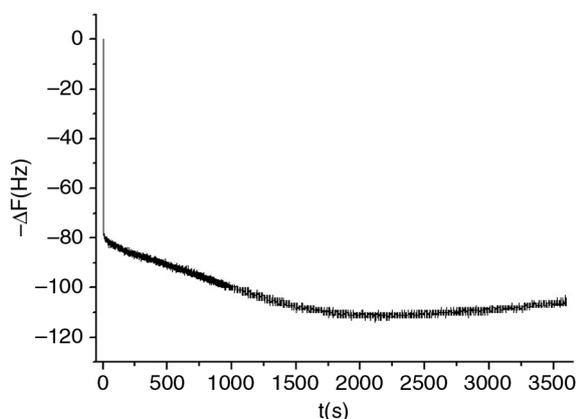


FIGURE 6. Frequency response over time of 1×10^{-3} M 2-MBT on copper.

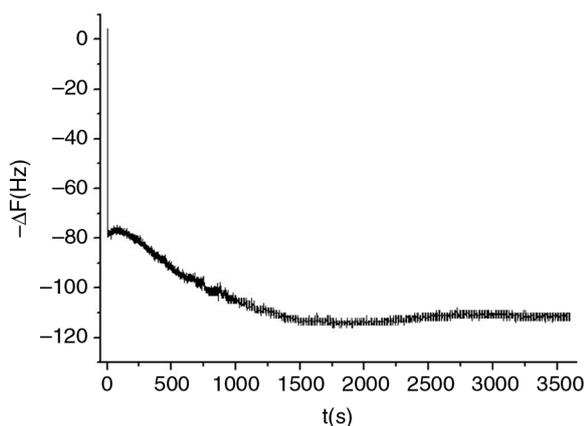


FIGURE 7. Frequency response over time of 1×10^{-6} M 2-MBT on copper.

The exponential behavior starts decaying at 2-MBT concentration 1×10^{-3} M (Fig. 4).

At 1×10^{-2} to 1×10^{-6} M 2-MBT concentrations (Fig. 3 to Fig. 7), an initial desorption process was

observed. This desorption process was attributed to the substitution of water molecules by 2-MBT molecules on the copper surface, according to the model described by Kern and Landolt (2001).

Desorption region increases as the concentration of 2-MBT decreases. It is clearly visible that a three step process takes place. In the first step 2-MBT molecules reach the metallic surface and force water molecules to desorb (initial desorption).

The second step is the adsorption of 2-MBT molecules at the active copper sites that are now vacant, due to the water desorption. It is considered that initially 2-MBT molecule is adsorbed in the metal surface through the exo-sulfur atom (Oshawa and Sütaka, 1979; Subramanian and Lakshminarayanan, 2002; Kazansky *et al.*, 2012; Ramenzanzadeh *et al.*, 2014) this fact is possible because 2-MBT molecules exhibit the thiol-thione tautomerism (Oshawa and Sütaka, 1979; Ramenzanzadeh *et al.*, 2014), in the range of pH of 3 to 9 (Jing *et al.*, 2013), which leads to an anionic form of 2-MBT (Winkler *et al.*, 2014) (Fig. 8).

The final step of the adsorption is the rearranging of 2-MBT molecules on the metal surface, as proposed in (Kokalj *et al.*, 2010), for molecules containing benzene rings. This molecule rearranging gives place to more water desorption, leaving unoccupied active sites on the metal surface, in the vicinity of the already adsorbed 2-MBT molecules.

Due to this fact, the new active sites are rapidly occupied by other inhibitor molecules available in the solution.

However, when 2-MBT concentration is too low (i.e., 1×10^{-4} to 1×10^{-6} M), there are not enough molecules to adsorb and compensate the mass loss, due to water desorption and thus, the resulting frequency response corresponds only to a desorption process (Fig. 5 to Fig. 7).

At concentration higher than 1×10^{-4} M 2-MBT (Fig. 2 to Fig. 4), there are enough inhibitor molecules to take the vacant sites left by water and therefore, no subsequent desorption is observed.

3.2. Adsorption isotherm

The frequency response of the three higher concentrations (1×10^{-1} up to 1×10^{-3} M 2-MBT) was fitted to the Langmuir kinetic model (Eq. 2). These concentrations were chosen because 2-MBT adsorption presents a well-defined exponential behavior (Figs. 2–4).

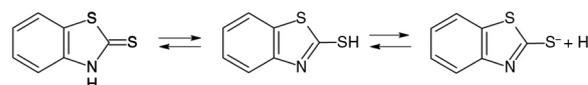


FIGURE 8. Thiol-Thione tautomeric equilibrium (Oshawa and Sütaka, 1979).

The fitted curves are presented in Figs. 9–11 and their respective calculated parameters are shown in Table 1.

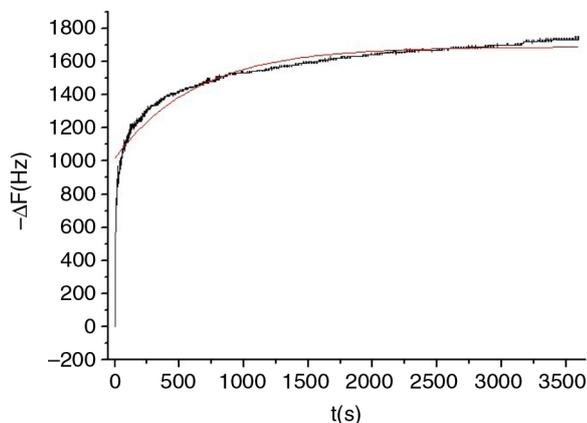


FIGURE 9. Fit of frequency response data to Langmuir adsorption isotherm (Eq. 2) of 1×10^{-1} M 2-MBT on copper.

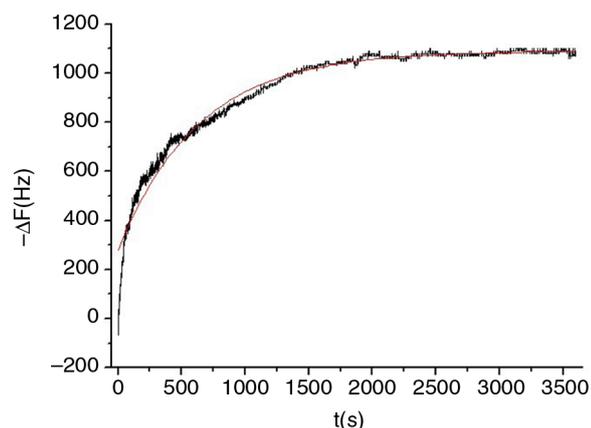


FIGURE 10. Fit of frequency response data to Langmuir adsorption isotherm (Eq. 2) of 1×10^{-2} M 2-MBT on copper.

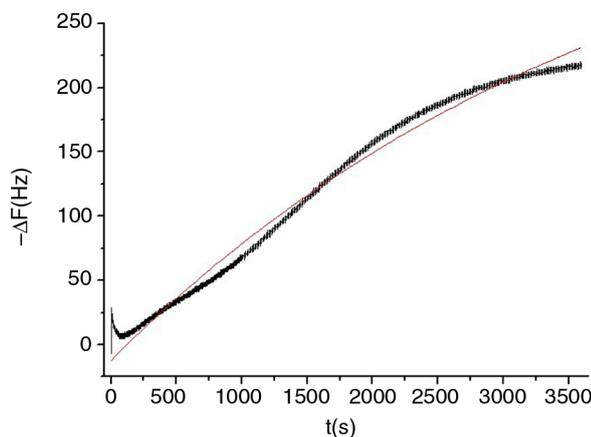


FIGURE 11. Fit of frequency response data to Langmuir adsorption isotherm (Eq. 2) of 1×10^{-3} M 2-MBT on copper.

TABLE 1. Langmuir fit parameters as a function of 2-MBT concentration [M]

2-MBT (M)	R ²	K'	k _m (s ⁻¹)	t ₀ (s)
1×10^{-1}	0.91	1689.40	1.60×10^{-3}	-575.94
1×10^{-2}	0.97	1090.64	1.58×10^{-3}	-186.56
1×10^{-3}	0.98	399.53	2.48×10^{-4}	120.48

The correlation coefficients show a very good agreement between the experimental data and the Langmuir isotherm. Figure 12 presents a plot of k_m vs C and its linear regression, which yields a k_a value of $8.21 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and a k_d value of $8.38 \times 10^{-4} \text{ s}^{-1}$.

Previously reported investigation (Karpovich and Blanchard, 1994) states that the negative deviation from linearity in the relation between k_m and C (for a thiol system, concentration range from 3×10^{-6} to 3×10^{-3} M) does not indicate that this system is ill-described by the Langmuir adsorption model. This fact only shows the intrinsic limits to this treatment of a complex equilibrium process. In other words, for low adsorbent concentration, the system remains in close proximity to equilibrium and the expected mass change for such conditions lies beneath our limit of detection.

3.3. Fraction of surface coverage (θ) and free energy of adsorption (ΔG_{ads})

According to equations 4 and 5, the equilibrium constant for 2-MBT adsorption process is $K_{eq}=9.79$, and the fraction of surface coverage (θ) values, as a function of adsorbent concentration, are shown in Table 2.

The free energy of adsorption was found to be $-5.59 \text{ kJ mol}^{-1}$. It is considered that a chemisorbed molecule must have a free energy of -40 kJ mol^{-1} (Atkins, 1999). Thus, the ΔG_{ads} energy found for

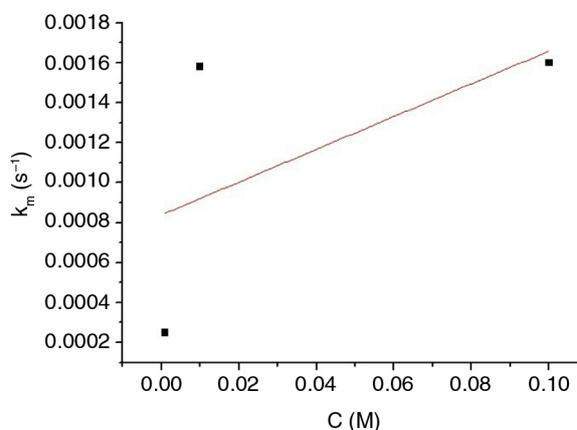


FIGURE 12. Linear fit for the concentration dependence of k_m .

TABLE 2. Fraction of surface coverage of copper surface

2-MBT (M)	θ
1×10^{-1}	0.50
1×10^{-2}	0.09
1×10^{-3}	0.01

2-MBT on copper surface clearly indicates that the adsorption is of physical nature, probably electrostatic.

4. CONCLUSIONS

2-MBT adsorbs on copper following the Langmuir adsorption isotherm. The initial desorption process observed in the concentration range 1×10^{-3} to 1×10^{-6} M is probably due to water molecules being substituted by 2-MBT molecules at the metal surface. The kinetic parameters of 2-MBT adsorption process showed a very low rate in the range of 2.48×10^{-4} to $1.60 \times 10^{-3} \text{ s}^{-1}$ and low surface coverage of 0.01 to 0.50. These facts are probably due to the lack of aggressive ions, which can deteriorate the copper patina, forming copper cations and exposing a pure metal surface to 2-MBT. Copper cations make possible the interaction with the anionic form of 2-MBT, leading to strong interactions, obtaining as a consequence higher adsorption rate and better surface coverage. Our research results showed that the calculated free energy of adsorption ($-5.59 \text{ kJ mol}^{-1}$) corresponds to a physisorption process, probably of electrostatic nature for the interaction between 2-MBT and copper surface in aqueous solution.

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