

## **SECM study of the pH distribution over Cu samples treated with 2-mercaptobenzothiazole in NaCl solution**

**J.A. Ramírez-Cano<sup>1</sup>, L. Veleva<sup>1\*</sup>, R.M. Souto<sup>2</sup>, B.M. Fernández-Pérez<sup>2</sup>**

<sup>1</sup>Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados (CINVESTAV), Unidad Mérida, km 6 Antigua carretera a Progreso, Apdo. Postal 73, Cordemex, 97310 Mérida, Yucatán, México

<sup>2</sup> Departamento de Química, Universidad de La Laguna, 38071 La Laguna, Tenerife, Islas Canarias, España.

\*Corresponding author: [veleva@cinvestav.mx](mailto:veleva@cinvestav.mx)

### **Abstract**

This paper reports the effect of treatment with 2-mercaptobenzothiazole (2MBT) (a corrosion inhibitor) on pH distribution over Cu samples monitored *in situ* using scanning electrochemical microscopy (SECM) in potentiometric mode. Line scans were conducted over two copper wires embedded in insulating resin, one of which had been pre-treated with 2MBT. It was found that the treated Cu sample had a less acidic character than the non-treated sample. Furthermore, the pH above the resin areas is considerably more acidic than that above either Cu wire. This feature is attributed to the consumption of OH<sup>-</sup> ions on the non-treated Cu wire during the formation of atacamite as a corrosion product, and the tautomeric equilibrium established by the detached 2-mercaptobenzothiazole molecules in the bulk electrolyte. These pH distributions are spatially resolved in the SECM mapping above both Cu wires.

**Keywords:** SECM; pH distribution; Copper; 2-Mercaptobenzothiazole; Atacamite; Multilayer film.

## 1. Introduction

The use of scanning electrochemical microscopy (SECM) to study the action of organic inhibitors on the metal corrosion process provides new insights into the complex processes occurring during the interaction between a metal and a corrosion inhibitor. A common approach to qualitative detection of corrosion activity on a metal substrate is to measure the local oxygen concentration [1,2], because this chemical species accepts the electrons lost by the metal atoms during their oxidation. The oxygen reduction reaction also has a considerable impact on the pH distribution in the system and so, using SECM in potentiometric mode, we can monitor the variation of the pH distribution on Cu samples *in situ*, and understand how the presence of inhibiting molecules at the surface changes the corrosion behavior of Cu in NaCl solution.

Scanning micro-electrochemical techniques are a very important branch of modern electrochemistry, with applications in a variety of different fields. One major use of methods such as the scanning vibrating electrode technique (SVET), scanning electrochemical microscopy (SECM), and localized electrochemical impedance spectroscopy (LEIS) is to provide information about the early stages of corrosion reactions [3-5]. In particular, the use of SECM enables the study of polymeric films on metals and their degradation dynamics [6,7], the selective dissolution of metals in alloys [8,9] and the formation and structural properties of protective films adsorbed over passive metal films [10,11]. SECM also has the additional advantage of its chemical selectivity [5], combined with spatial resolution, which can help elucidate the electrochemical processes involved in corrosion phenomena.

In this work we report on the effect of pre-treating Cu samples with 2-mercaptobenzothiazole (2MBT), a well-known corrosion inhibitor for this metal [12-17], on the pH distribution above the samples. The samples were immersed in NaCl aqueous solution and measurements were made using a scanning electrochemical microscope (SECM) operated in potentiometric mode [18, 19].

## 2. Experimental

### 2.1. Preparation of Materials

Two copper wires (purity >99.99%, diameter 125  $\mu\text{m}$ ) were mounted into an Epofix epoxy resin (Struers, Ballerup, Denmark) circular mold with a separation between the wires of approximately 1.8 mm. Their cross-section separated by epoxy resin was used as the sampling area, while the electrical contact of the copper wires was at the rear of the mold. The inhibitor, 2-mercaptobenzothiazole (2MBT, Aldrich, 96%), was used as received to prepare 1 mM aqueous solution in bi-distilled water (conductivity 18.2  $\text{M}\Omega\text{ cm}$ ), employing a sonicator to dissolve the organic compound due to its low solubility in water.

The samples embedded in epoxy resin were ground with silicon carbide paper to 4000 grit and polished with 0.3  $\mu\text{m}$  alumina slurry. The resulting surface was rinsed with ethanol and kept in a bath containing ethanol until the inhibitor treatment was applied. The inhibitor was applied to only one of the two Cu wires in the mold; the other was used as a control sample. The inhibitor pre-treatment consisted in placing a 10  $\mu\text{L}$  volume droplet of 1 mM 2MBT solution over the cross-section of the Cu wire for one hour, and then removing it using a micropipette.

### 2.2. Electrochemical characterization

After treatment with the inhibitor, the sample was transferred to the SECM instrument, and a small container for the test solution (volume  $\approx$  3.5 mL of 1 mM NaCl; pH 6.76) was created by surrounding the epoxy resin mold with Sellotape. The microelectrodes for potentiometric SECM operation were introduced into this electrochemical cell. These comprised a Sb microelectrode as working electrode with a 30  $\mu\text{m}$  active disk surface and Ag/AgCl/KCl (3M) as reference electrode. The fabrication of the microelectrodes has been described elsewhere [19].

Calibration of the Sb microelectrode tip showed a linear relationship between potential and the solution pH, with a slope of  $-48.6\text{ mV pH}^{-1}$  in the  $4 \leq \text{pH} \leq 11$  range. This linear relationship makes it possible to determine if the response of the tip corresponds to

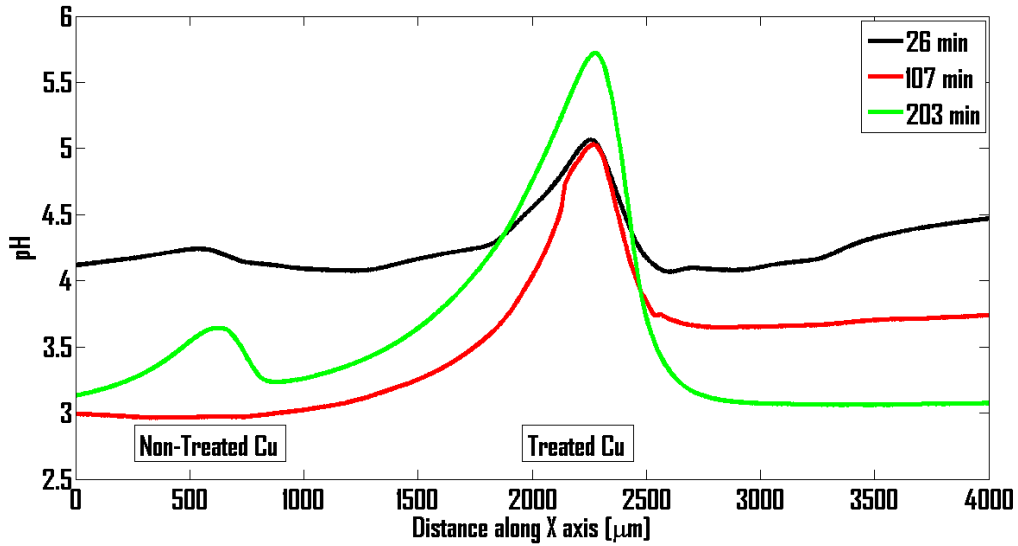
Nernstian behavior in buffer solutions. This is only an indication of the viability of the tip as an electrochemical sensor. In [19] the tip was calibrated in the  $3 < \text{pH} < 11.5$  range with a very similar slope to the one obtained in this work, confirming Nernstian behavior even over this extended range. SECM imaging was performed either as bidimensional maps or as line scans.

The maps were recorded at a height of  $30 \mu\text{m}$  from the sample with a scan rate of  $60 \mu\text{m s}^{-1}$  (step size  $60 \mu\text{m}$ ), extending over an area of  $3000 \mu\text{m} \times 1500 \mu\text{m}$  containing the two copper wires surrounded by the epoxy resin. Line scans passing over the centers of the two copper wires were performed at the same height with a line length of  $4000 \mu\text{m}$  and a scan rate of  $10 \mu\text{m s}^{-1}$ . No perturbation was caused to the system.

### 3. Results and discussion

Fig. 1 shows a selection of the pH distributions obtained during the line scans for various times of immersion in  $1 \text{ mM NaCl}$ . It can be seen that the Cu wire treated with 2MBT has a less acidic character, with a pH value of 5.06 after 26 minutes of immersion, and reaches a maximum pH value of 5.72 after 203 minutes. However, the non-treated sample displays a lower pH value of 4.24 after 26 minutes, becoming more acidic after 107 minutes with a registered pH of 2.97. Finally, after 203 minutes the pH of the non-treated sample becomes slightly less acidic, with a final recorded pH value of 3.64.

During the first scan (Fig. 1), recorded at 26 minutes, the pH of the electrolyte above the resin areas and the non-treated copper wire (i.e., 4.12–4.77) is almost one pH unit more acidic than above the area of the 2MBT-treated Cu sample (5.06). However, after 107 minutes the pH values on the resin lay between 2.99 and 3.74. In the last scan recorded after 203 minutes the corresponding values were 3.07–3.14. In the last scan, a less acidic environment can be noticed over the non-treated copper wire, though this is still 2 pH units less alkaline than the Cu wire modified with 2MBT.



**Fig. 1.** Potentiometric SECM line scans depicting the pH distributions generated in the electrolyte adjacent to 2MBT-treated (right) and non-treated (left) Cu wires in 1 mM NaCl. Sensing tip: Sb disc, 30  $\mu\text{m}$  diameter; tip-substrate distance: 30  $\mu\text{m}$ ; scan direction: from right to left; scan rate: 10  $\mu\text{m s}^{-1}$ .

The corrosion behavior of copper in NaCl solution has been widely studied. The cathodic reaction of copper in NaCl solution is oxygen reduction [20-22]:



On the other hand, the dissolution at the anode is a complex process that involves a series of reactions [20,22,23]:



This reaction mechanism can lead to the formation of atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ) as follows:



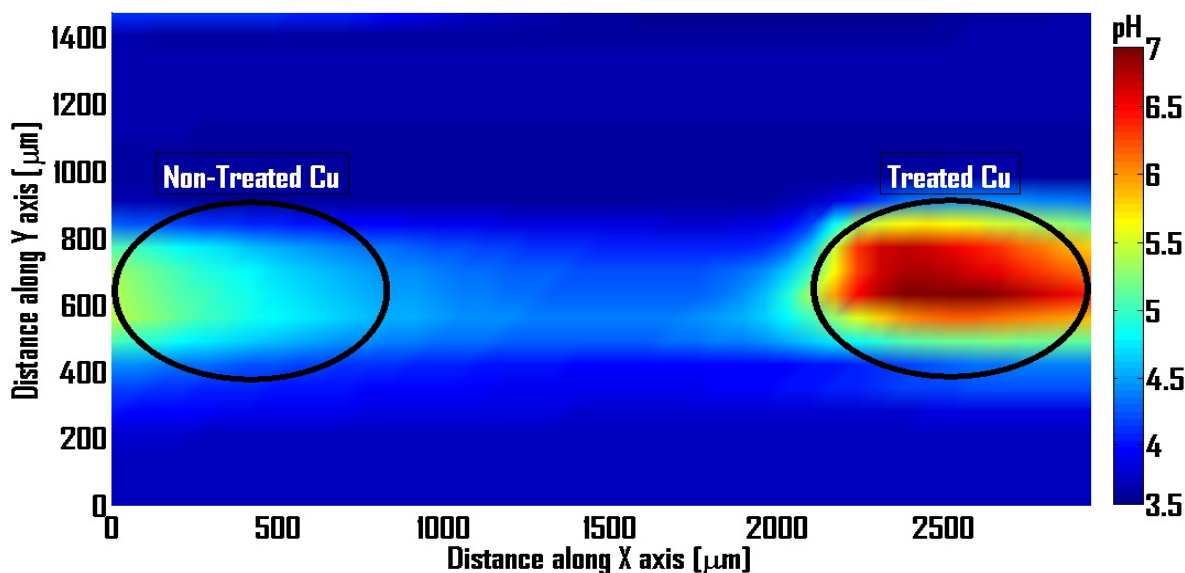
The consumption of  $\text{OH}^-$  during the formation of atacamite could explain to some extent the acidification of the electrolyte around the non-treated Cu surface which is acting as the anode in the corrosion cell.

The treated (inhibitor-modified) Cu sample is acting as the cathode, and therefore oxygen reduction (Eq. 1) takes place on its surface. This will turn the pH of its immediate vicinity considerably more alkaline than the rest of the system. According to equation 1, OH<sup>-</sup> ions are formed at the cathodic site and these are consumed at the anodic site (Eq. 5). The final result is a pH in the neutral range, which was observed in the map (Fig. 2).

Similar behavior is observed in Fig. 2, which shows the SECM mapping of both Cu wires recorded after immersion for 1 hour. The inhibitor-treated Cu wire shows a more alkaline pH (namely, 7.0), corresponding to the consumption of oxygen at the cathode, while the non-treated sample displays a more acid pH value that varies between 4.5 and 5.5, because copper is corroding (Eq. 5).

The apparent discrepancies in the pH values observed between Fig. 1 and Fig. 2 can be explained in terms of the size of the area scanned. While Fig. 1 corresponds to line scans, which have a width of 30 μm, Fig. 2 describes a map which is a collection of lines. These lines represent different areas of the sample (i.e., they extend over a number of anodic and cathodic sites).

As noted before, the consumption of hydroxide ions during atacamite formation partially explains the acidification of the NaCl solution. However, there is another possible explanation for this phenomenon that is related to the presence of 2MBT. It is likely that the protective film adsorbed on the Cu surface is a multilayer structure rather than an ordered and stable monolayer. The inhibitor 2-mercaptobenzothiazole is a tautomer that has a tautomeric equilibrium in the pH range 3–9 [24,25]. This suggests deprotonation of the molecule and subsequent acidification of the media in which it occurs (the NaCl solution in this case). The presence of a multilayer film would lead to the detachment of the outermost molecules of the film which, once in the bulk solution, would deprotonate as part of their tautomeric equilibrium, leading to the acidification observed over the resin areas.



**Fig. 2** Potentiometric SECM scan map showing the pH distribution in a plane parallel to the surface of the Cu wires after immersion in 1mM NaCl for 1 h. Sensing tip: Sb disc, 30  $\mu\text{m}$  diameter; tip–substrate distance: 30  $\mu\text{m}$ ; scan rate: 60  $\mu\text{m s}^{-1}$ .

To support the idea of a multilayer structure, we can estimate the number of molecules that are needed to create a monolayer. To do this, we will use data from a previously published work by the authors [16] in which, employing the electrochemical quartz crystal microbalance (EQCM), the frequency variation during 1 mM 2MBT adsorption on copper was obtained ( $\Delta f = -225$  Hz).

By using the Sauerbrey equation (Eq. 6), with a sensitivity factor ( $C_f$ ) of 226 Hz  $\text{cm}^2 \mu\text{g}^{-1}$ , the amount of adsorbed mass per square centimeter ( $\Delta m$ ) can be estimated. Multiplying this amount by the active area of 0.205  $\text{cm}^2$ , a total adsorbed mass of 0.203  $\mu\text{g}$  is obtained. Considering that a 2MBT molecule has an approximate mass of  $2.77 \times 10^{-22}$  g, the number of adsorbed molecules on the copper surface is found to be  $7.29 \times 10^{14}$ . Using the density of 2MBT (1.42  $\text{g cm}^{-3}$ , according to Sigma Aldrich) the volume of the adsorbed film can be estimated, yielding  $1.42 \times 10^{-7}$   $\text{cm}^3$ . Assuming that a uniform film is created, a film thickness of 6.92 nm is obtained.

$$\Delta f = -C_f \Delta m \quad (6)$$

On the other hand, the volume of a 2MBT monolayer can be estimated assuming that the molecule is planar and that its adsorption orientation is with the benzene ring parallel to

the Cu surface. This adsorption orientation has been seen previously for similar compounds [22,26]. Taking the atomic diameter of the more abundant atom in the molecule (2MBT,  $C_7H_5NS_2$ ) which is carbon with an approximate atomic diameter of 182 pm or  $1.82 \times 10^{-8}$  m [26] as the thickness of the monolayer, a volume of  $3.73 \times 10^{-9}$  cm<sup>3</sup> is obtained. Using the density of 2MBT and the mass of a single molecule of 2MBT, the volume of a single 2MBT molecule can be estimated ( $1.95 \times 10^{-22}$  cm<sup>3</sup>).

Therefore, a monolayer of 2MBT over the Cu active area of 0.205 cm<sup>2</sup> (of the EQCM electrode) will require  $1.91 \times 10^{13}$  2MBT molecules. Since there are  $7.29 \times 10^{14}$  molecules adsorbed, it is reasonable to assume that the film formed on copper has a multilayer structure. Furthermore, the adsorption free energy ( $\Delta G_{ads} = -5.59$  kJ mol<sup>-1</sup>) was also calculated [16]. This value corresponds to a physisorption process leading to weak bonding and a more unstable adsorption of the outermost molecules. These could then detach and deprotonate, resulting in the acidification of the adjacent electrolyte (Fig. 2).

#### **4. Conclusions**

The use of SECM in potentiometric mode makes it possible to image the pH distributions produced in the surrounding electrolyte by the interaction of 2-mercaptobenzothiazole with copper. Since corrosion processes are highly sensitive to pH, local pH effects associated with the interaction between inhibitor molecules and the metal are of major importance. In this work it has been demonstrated that the presence of an adsorbed film of 2MBT on the surface of a Cu sample can produce a pH shift towards more alkaline values in a small volume of 1 mM NaCl solution, compared to a non-treated Cu surface. This is due to the presence of a protective film of 2MBT on the Cu surface, which effectively inhibits metal dissolution, but may still act as the cathode (where the oxygen reduction takes place) in the corrosion cell formed when in electrical contact with non-treated copper. Meanwhile, copper dissolution and atacamite formation occur at the non-inhibited sample, which displays a more acidic pH value due to the consumption of OH<sup>-</sup> during the anodic process.



Further acidification is attributed to the detachment of 2MBT molecules from the multilayer film adsorbed on inhibitor-treated Cu. These molecules participate in a tautomeric equilibrium that involves the deprotonation of the molecules in the bulk of the solution, leading to a noticeable acidification of the NaCl solution that extends over the surrounding resin areas.

### **Acknowledgements**

The authors would like to express their gratitude to the National Council of Science and Technology of México (CONACYT) for the scholarship no. 290936 granted to J.A. Ramírez-Cano to carry out a research stay at the Universidad de La Laguna (Spain).

### **References**

- [1] R.M. Souto, L. Fernández-Mérida, S. González, SECM imaging of interfacial processes in defective organic coatings applied on metallic substrates using oxygen as redox mediator, *Electroanalysis* 21 (2009) 2640-2646.
- [2] L.C. Abodi, Y. Gonzalez-Garcia, O. Dolgikh, C. Dan, D. Deconinck, J.M.C. de Mol, H. Terryn, J. Deconinck, Simulated and measured response of oxygen SECM-measurements in presence of a corrosion process, *Electrochim. Acta* 146 (2014) 556-563.
- [3] Y. González-García, G.T. Burstein, S. González, R.M. Souto, Imaging metastable pits on austenitic stainless steel in situ at the open circuit corrosion potential, *Electrochem. Commun.* 6 (2004) 637-642.
- [4] R.S. Lillard, Scanning electrode techniques for investigating near-surface solution current densities, in: P. Marcus, F. Mansfeld (Eds.), *Analytical Methods in Corrosion Science and Engineering*, CRC Press, Boca Raton, FL, 2006, pp. 571-604.
- [5] M.B. Jensen, D.E. Tallman, Application of SECM to corrosion studies, in: A.J. Bard, C.G. Zoski (Eds.), *Electroanalytical Chemistry, A Series of Advances*, Vol.24, CRC Press, Boca Raton, FL, 2012, pp.171-286.

- [6] R.M. Souto, Y. González-García, S. González, G.T. Burstein, Damage to paint coatings caused by electrolyte immersion as observed in situ by scanning electrochemical microscopy, *Corros. Sci.* 46 (2004) 2621-2628.
- [7] R.M. Souto, Y. González-García, S. González, Characterization of coating systems by scanning electrochemical microscopy: Surface topology and blistering, *Prog. Org. Coat.* 65 (2009) 435-439.
- [8] A.M. Simões, A.C. Bastos, M.G. Ferreira, Y. González-García, S. González, R.M. Souto, Use of SVET and SECM to study the galvanic corrosion of an iron–zinc cell, *Corros. Sci.* 49 (2007) 726-739.
- [9] J. Izquierdo, L. Nagy, S. González, J.J. Santana, G. Nagy, R.M. Souto, Resolution of the apparent experimental discrepancies observed between SVET and SECM for the characterization of galvanic corrosion reactions, *Electrochem. Commun.* 27 (2013) 50-53.
- [10] J. Izquierdo, J.J. Santana, S. González, R.M. Souto, Uses of scanning electrochemical microscopy for the characterization of thin inhibitor films on reactive metals: The protection of copper surfaces by benzotriazole, *Electrochim. Acta* 55 (2010) 8791-8800.
- [11] J. Izquierdo, J.J. Santana, S. González, R.M. Souto, Scanning microelectrochemical characterization of the anti-corrosion performance of inhibitor films formed by 2-mercaptobenzimidazole on copper, *Prog. Org. Coat.* 74 (2012) 526-533.
- [12] M. Finšgar, D.K. Merl, An electrochemical, long-term immersion, and XPS study of 2-mercaptobenzothiazole as a copper corrosion inhibitor in chloride solution, *Corros. Sci.* 83 (2014) 164-175.
- [13] J.C. Marconato, L.O. Bulhões, M.L. Temperini, A spectroelectrochemical study of the inhibition of the electrode process on copper by 2-mercaptobenzothiazole in ethanolic solutions, *Electrochim. Acta* 43 (1998) 771-780.
- [14] M. Ohsawa, W. Suëtaka, Spectro-electrochemical studies of the corrosion inhibition of copper by mercaptobenzothiazole, *Corros. Sci.* 19 (1979) 709-722.

[15] R. Subramanian, V. Lakshminarayanan, Effect of adsorption of some azoles on copper passivation in alkaline medium, *Corros. Sci.* 44 (2002) 535-554.

[16] J.A. Ramírez Cano, L. Veleza, Direct measurement of the adsorption kinetics of 2-mercaptobenzothiazole on a microcrystalline copper surface, *Rev. Metal.* 52(1) (2016) 11-12. DOI: 10.3989/revmetalm.064

<http://revistademetalurgia.revistas.csic.es/index.php/revistademetalurgia/article/view/1377>

[17] M.M. Antonijevic, M.B. Petrovic, Copper corrosion inhibitors. A review, *Int. J. Electrochem. Sci.* 3 (2008) 1-28.

[18] B. Csóka, B. Kovács, G. Nagy, Investigation of concentration profiles inside operating biocatalytic sensors with scanning electrochemical microscopy (SECM), *Biosens. Bioelectron.* 18 (2003) 141-149.

[19] J. Izquierdo, L. Nagy, Á. Varga, J.J. Santana, G. Nagy, R.M. Souto, Spatially resolved measurement of electrochemical activity and pH distributions in corrosion processes by scanning electrochemical microscopy using antimony microelectrode tips, *Electrochim. Acta* 56 (2011) 8846-8850.

[20] Y. Qiang, S. Zhang, S. Xu, L. Yin, The effect of 5-nitroindazole as an inhibitor for the corrosion of copper in a 3.0% NaCl solution, *RSC Adv.* 5 (2015) 63866-63873.

[21] B. Hammouti, A. Dafali, R. Touzani, M. Bouachrine, Inhibition of copper corrosion by bipyrazole compound in aerated 3% NaCl, *J. Saudi. Chem. Soc.* 16 (2012) 413-418.

[22] Y. Qiang, S. Zhang, S. Xu, W. Li, Experimental and theoretical studies on the corrosion inhibition of copper by two indazole derivatives in 3.0% NaCl solution, *J. Colloid. Interf. Sci.* 472 (2016) 52-59.

- [23] S. Ogata, N. Kobayashi, T. Kitagawa, S. Shima, A. Fukunaga, C. Takatoh, T. Fukuma, Nanoscale corrosion behavior of polycrystalline copper fine wires in dilute NaCl solution investigated by in-situ atomic force microscopy, *Corros. Sci.* 105 (2016) 177-182.
- [24] M. Ohsawa, W. Suëtaka, Spectro-electrochemical studies of the corrosion inhibition of copper by mercaptobenzothiazole, *Corros. Sci.* 19 (1979) 709-722.
- [25] P. Jing, M. Hou, P. Zhao, X. Tang, H. Wan, Adsorption of 2-mercaptobenzothiazole from aqueous solution by organo-bentonite, *J. Environ. Sci.* 25 (2013) 1139-1144.
- [26] A. Kokalj, S. Peljhan, M. Finšgar, I. Milošev, What determines the inhibition effectiveness of ATA, BTAH and BTAOH corrosion inhibitors on copper, *J. Am. Chem. Soc.* 132 (2010) 16657-16668.
- [27] R. Chang, *Chemistry*, Mc Graw Hill Education, Columbus, OH, 2002, pp. 297-298.