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Methods for Characterization of Protective Films on the Copper Surface - A Review

Formation of protective film on the copper surface and characterization of metal surface was the major subject of interest. In this paper was presented resolution in this field. Also, in paper was pay attention on methods which were used in investigation especially in the previous few years. According to the summarized results, described methods gave useful information about formation of protective film, which can block the dissolution of copper and its effectiveness, afterwards about strength of the bonds between atoms, corrosion inhibition mechanism, surface structure and adsorbed species on the metal surface. Inhibitors were mostly chemisorbed on the copper surface through different bond while presence of different group had influence on the inhibitor efficiency. Also, different types of bonds on the copper surface in the solution with different inhibitors were noticed.

Key words: *corrosion inhibitors, EIS, XPS, FT-IR, SERS*

INTRODUCTION

Copper and its alloys have a great importance for modern life and many industries. Copper plays an increasingly important role in the newest development of chip design for the computer and microelectronic industry [1]. Copper application based on its good thermal and electrical conductivity, mechanical properties and relatively noble properties [2]. Exactly these characteristics enable application in the aggressive circles. Scientists and engineers utilize a numerous methods to prevent collapse of these materials. Organic compounds which containing polar groups including nitrogen, sulfur, and oxygen, and heterocyclic compounds with polar functional groups and conjugated double bonds have been reported to inhibit copper corrosion [3-5]. The inhibition of these organic compounds is usually attributed to their interactions with the copper surface via their adsorption [6,7]. Organic compound like azoles have shown high efficiency as a corrosion inhibitor for copper and copper-based alloys in different environmental [7,8]. Of particular interest in the general field of organic inhibitors are the nature of the chemical bond at the metal surface and an explanation of why these substances often provide such excellent protection [9]. Compounds with π-bonds also generally exhibit good inhibitive properties due to interaction of π orbital with metal surface. Rhe presence of unoccupied π^*-orbitals in the Sshiff base molecule, which enable electron back-donation from the transition metal d-orbitals and stabilize the existing metal-inhibitor bond, causes the Schiff bases to display considerable corrosion inhibition efficiencies [10]. Many compound build protective layer on the metal surface. Heterocyclic compound such as benzotriazole [9, 11 - 14], thiazole [15], triazole [16], tetrazole [17], imidazole [18] and their derivates are the most common inhibitors used in the battle against copper corrosion and its alloys in aqueous solutions. Benzotriazole is one of the most often applied

inhibitor. Because of that BTA is the mostly tested in the different solution [8,19,20]. The effectiveness of these heterocyclic molecules is based on their ability to form a polymerlike film, which prevents copper corrosion [21-23]. Understandings of nature and structure of protective film are very important for further development in the protection of metals. Scientists used a large number of different techniques for complete understanding of inhibition mechanism and for complete image of protective layer structure. Some of those techniques are electrochemical [4,24,25], photoelectrochemical [12,26], spectroscopic [24,27], but all applied techniques have purpose which we mention above. Organic self-assembled monolayers (SAM) on various metal surfaces have drawn increasing interest because of the spontaneous formation of highly ordered and compact thin films [28]. One of the most used electrochemical techniques is electrochemical impedance spectroscopy [29-31]. Other methods which have great importance are: X-ray photoelectron spectroscopy [32-34], Fourier transform infrared spectroscopy (FT-IR) [16,35,36], surface enhanced Raman scattering (SERS) [28,29], scanning tunneling microscopy [1,37,38].

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY MEASUREMENTS

Electrochemical impedance spectroscopy is one of the most often used methods which were successfully benefited to explain corrosion process and inhibition of metals in different solutions [39]. EIS provided an effective method for measuring the resistance against the transfer of ionic species to the underlying metal surface, and it has been widely used to evaluate the barrier properties of inhibitors [23]. This method was employed for surface layer thickness examines [2]. The electrochemical impedance spectroscopy provides important mechanistic and kinetic information for an electrochemical system under investigation [40]. Also, EIS measurement was carried out to determine kinetic parameters for electron transfer reaction at the copper/electrolyte interface [3]. Electrochemical impedance spectroscopy is an electrochemical measurement technique
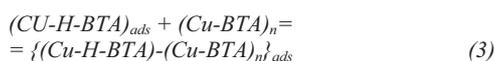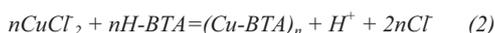
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which can directly measure the solution resistance (R_S), the charge-transfer resistance (R_{ct}), and the double-layer capacitance (C_{dl}). From R_{ct} and the corresponding formula, the film coverage (θ) on the electrode can be calculated. The film coverage reflects the assembly effect of the film. The double-layer capacitance can also be used to determine the quality of a film [41].

Sherif et al. [39] investigated influence of 3-amino-1,2,4-triazole (ATA) on the inhibition of copper corrosion in the HCl solution. Electrochemical impedance spectroscopy was one method which had great used in that investigation. They were found that the presence of ATA and the increase of its concentration raised the impedance values over the whole frequency range. These kinds of results indicate the passivation of the copper surface and confirm the ability of ATA to protect copper forming a protective layer on the copper surface.

Guilminot et al. [13] used EIS to evaluate the effectiveness of BTA in an aqueous solution of polyethylene glycol (PEG). The impedance spectra plotted in the presence of BTA and without the BTA are identical. The action mechanism of BTA on the copper includes an adsorption phase, so there is a risk of competitive adsorption between the BTA and the PEG on the surface. BTA reduced the number of active sites on the metal surface and formed a more protective layer than the PEG. Benzotriazole was adsorbed on the metal surface and formed complex Cu(I)/BTA, Cu(II)BTA.

It is generally accepted that the inhibition mechanism of BTA is the formation of a polymeric film of a CuBTA on the copper surface. The inhibition efficiency of the CuBTA film was strongly dependent on the degree of its polymerization, and a higher degree of polymerization of the film caused better inhibition efficiency [9]. A Cu-BTA film formation in a chloride solution path was proposed as follows [19]:

$$Cu + H\text{-}BTA = (Cu\text{-}H\text{-}BTA)_{ads} \qquad (1)$$

$$nCuCl_2 + nH\text{-}BTA = (Cu\text{-}BTA)_n + H^+ + 2nCl^- \qquad (2)$$

$$\begin{aligned}(CU\text{-}H\text{-}BTA)_{ads} + (Cu\text{-}BTA)_n = \\ = \{(Cu\text{-}H\text{-}BTA)\text{-}(Cu\text{-}BTA)_n\}_{ads}\end{aligned} \qquad (3)$$

Zhang et al. [9] investigated influence of bis-(1-benzotriazolymethylene)-(2,5-thiadiazoly)-disulfide (BBTD) on the copper corrosion in chloride solution using EIS. Result were indicated that anodic oxidation process on the copper surface provoked Warburg impedance which indicating a diffusion effect. Also, was evident that BBTD was formed protective layer on the metal surface.

Sherif and Park [6] investigated the effect of the 2-amino-5-(ethylthio)-1,3,4-thiadiazole (ATD) in 0,5M HCl. They followed total polarization resistance as a function of the inhibitor concentration and found that the total polarization resistance is linearly related to the inhibitor concentration. This indicated that the inhibitor forms a layer, which grows upon increasing the inhibitor concentration and behaves as a resistor for the electron transfer. The layer was become thicker in direct proportion to the concentration of inhibitor. Authors draw a conclusion that Warburg impedance indicated that the mass transport limited

the access of the reactants through the adsorbed layer on the copper surface.

Abelev et al. [23] followed formation of the protective layer on the copper surface in sulphate solution with n-alkanoic acid potassium salts. The properties of the surface film were characterized by the layer resistance which reflected the protective properties of the carboxylate-modified copper film. Copper immersed in solution media containing n-alkanoic acid potassium salts with a chain length than six carbons has been observed to develop hydrophobic surface films at the copper surface. The length of the hydrocarbon chain has a dramatic influence on copper corrosion protection. Longer hydrocarbon chain lengths provide better corrosion protection. The same authors investigated influence of immersion time on the formation of protective layer on the copper surface. Results indicated that the formation of an enhanced protective film at electrode surface with a longer exposure time of the copper electrode.

Sherif and Park [3] investigated influence of N-phenyl-1,4-phenylenediamine on the copper corrosion in deaerated, aerated and oxygenated aqueous 0,5M HCl solutions using different methods. Results indicated that the adsorbed NPPD layer on the metal surface blocks the mass transport acting like a resistor. The EIS measurements have also revealed that the surface and charge transfer resistances are increased upon addition of inhibitor. The inhibition efficiency was calculated from the charge transfer resistance as follows:

$$IE\% = \left[\frac{R_{p1} - R_{p2}}{R_{p1}}\right] \times 100 \qquad (4)$$

Here R_{p1} and R_{p2} are the charge transfer resistance with and without inhibitor present, respectively. The IE% values increased upon addition of inhibitor in all solution (table 1).

Table 1 - Inhibition efficiency of inhibitors in the chloride solution

Solution	C_{inh}	IE[%]	References
HCl + AETD	1mM	54,8	Sherif and Park [6]
HCl + AETD	5mM	70,8	
HCl + AETD	10mM	78,5	
De-aerated NaCl + AETDA	1×10^{-3}M	84	Sherif and Park [42]
De-aerated NaCl + AETDA	5×10^{-3}M	95	
Aerated NaCl + AETDA	1×10^{-3}M	87,9	
Aerated NaCl + AETDA	5×10^{-3}M	99	
Oxygenated NaCl + AETDA	1×10^{-3}M	93,8	
Oxygenated NaCl + AETDA	5×10^{-3}M	99,6	
De-aerated HCl + NPPD	1mM	48,3	Sherif and Park [3]
De-aerated HCl + NPPD	5mM	66,6	
De-aerated HCl + NPPD	10mM	79,8	
Aerated HCl + NPPD	1mM	44,7	
Aerated HCl + NPPD	5mM	64,2	
Aerated HCl + NPPD	10mM	73,6	
Oxygenated HCl + NPPD	1mM	45,1	
Oxygenated HCl + NPPD	5mM	71,1	
Oxygenated HCl + NPPD	10mM	83	

Huynh et al. [29] investigated the inhibitive effect of carboxybenzotriazole in solution of alkyl esters. Impedance spectra showed that the film formed by pretreatment in aqueous solution of inhibitors can be stable in acidic sulphate solution (pH=0) up to 3 days. Results also show that the esters film formed on the metal surfaces become more protective as the alkyl chain made longer. In the other work Huynh et al. [43] interrogated the thickness of the protective film on the copper surface in the sulphate solution with a derivative of carboxybenzotriazole. Thickness was been calculated by the expression:

$$d = \varepsilon_o \varepsilon_r A / C \qquad (5)$$

Where ε_o-vacuum permeability, ε_r-dielectric constant of the film, A-area of electrode, C-film's capacitance. EIS measurements point to that the corrosion resistance of the film is increased as the alkyl chain length of the inhibitor made longer. Results of the measurements indicated that protective film was formed on the electrode surface. Also, results indicate that IE depends on the length of the alkyl chain. The presence of Warburg impedance indicates that there is diffusion of electrolyte through pores in the inhibitor films. The decrease of the ratio W/R_L (Warburg impedance/Resistance of the layer) with increase in exposure time can be related to the decrease in the number of pores or defective sites as the film is built up on the copper surface.

Table 2 - Dependence of film coverage of time in chloride solution with addition of inhibitors

Solution	Immersion time [h]	θ [%]	References
HCl + ATA	6	57-65	Sherif et al. /39/
	12	57-65	
	18	57-66	
	24	58-67	
	30	59-68	
	36	60-68	
	42	60-70	
	48	60-71	
NaCl + TEP	1	81	Guo et al. /41/
	4	90,2	
	12	93,8	
	24	85,3	
NaCl + TPP	1	85,4	
	4	88,1	
	12	96,5	
	24	93,1	

Guo et al. [41] investigated the inhibition effects of triethyl phosphate and triphenyl phosphate of the copper corrosion in 0,2M NaCl solution using EIS. EIS measurements appeared that the mass transfer limited diffusion rate of $CuCl_2^-$ complexed species, while the anodic diffusion process mainly involves the diffusion of soluble copper species from the surface of the electrode to the bulk solution. When the electrode surface was covered with a film, the value of R_{ct} increased rapidly. In fact, SAMs formed at the electrode surface can act as a barrier layer between the electrode and the solution and efficiently hinder the attack of the substrate by chloride ions. The disappearance of the Warburg impedance may imply the formation of better films coated on the electrode. The film coverage can be calculated from the following formula:

$$(1-\theta) = \frac{R_{ct}^o}{R_{ct}} \qquad (6)$$

Where R_{ct}^o is the charge-transfer resistance of the naked electrode and R_{ct} is the charge-transfer resistance of a copper electrode covered with SAMs. The increase of film coverage can reflect the increase of the number of the molecules adsorbed on Cu and the improvement of the inhibition effect. The inhibition effect is better when immersion time increase (table 2).

FOURIER TRANSFORM INFRARED SPECTROSCOPY INVESTIGATION

Fourier Transform Infrared Spectroscopy is technique which is used to define surface characterization. Infrared spectroscopy is a technique which can give to us information about adsorption geometry and this surface analytical technique is very sensitive and has a great usage [44]. The FT-IR measurements provide information concerning both the strength of the bonds between atoms and the structure of the molecule [9,25].

Lalitha et al. [16] investigated influence of some triazole compound and some ionic surfactants on the corrosion control of the copper in acidic solutions. Triazole compound which were used: 3-amino 1,2,4 triazole (ATA), 3-amino 5-mercapto 1,2,4 triazole (AMT), 3-amino 5-methylthio 1,2,4 triazole (AMTT). Cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) were the ionic surfactants which were used. The interaction between the organic compounds and the metal surfaces has been studied by means of FT-IR reflection spectra. FT-IR spectra pointed to formation of bonds between molecules in the system which indicated to the chemisorption of inhibitors on the metal surface through nitrogen atom.

Vogt et al. [44] followed the adsorption of benzotriazole on Cu(100) electrode in 0,1M HCl solution. Infrared spectroscopy experiments were performed with a purpose to confirm a formation of a Cu(I)BTA layer on the metal surface. Results have showed that no changes in the potential range between -0,7 and -0,3V. At potentials higher than -0,3V several bands arise in the region between 1350 and 1000cm^{-1}. This indicated that the Cu(I)BTA complex formed at positive potential was adsorbed on the copper surface, but also indicates that concentration of BTA in the thin layer decrease above -0,3V.

Zhang et al. [9] used FT-IR spectra to confirm formation of BBTD-Cu(I) complex in NaCl solution with addition of bis-(1-benzotriazolymethylene)-(2,5-thiadiazoly)-disulfide. Results leaded investigators to conclusion that surface complex could be identified as BBTD-Cu(I). BBTD molecules may be chemisorbed on the copper surface and rapidly react with Cu(I) on or around the copper surface to form the [BBTD-Cu(I)-H$_2$O] complexes on the copper surface.

Ramesh and Rajeswari [2] used FT-IR spectra to determinate structure of the protective film formed on the metal surface in the lake water with addition of 4ppm of 3-salicylalidene amino 1,2,4-triazole phosphonate (SATP) and with addition of 4ppm of 3-salicylalidene amino 1,2,4-triazole phosphonate + 5ppm of molybdate + 15ppm of 3-cinnamalidene amino 1,2,4-triazole phosphonate (SATP++Mo+CTAB). In the FT-IR spectra were identified P=O bonds, P-O and P-OH stretch. The P-O bond disappeared in the solution with SATP and with SATP + Mo + CTAB. This can be attributed to a P-O-M bond in which a free P^+-O^- interact with metallic species. P-OH streatching is week further indicates the possibility of a P-O-Cu bond. Results unambiguous showed that the polymeric complex was formed by covalent and coordinate covalent bonds. The formation of a complex is the result of the reaction between the triazole ring and the metal surface. In this case it may be viewed as a result of Lewis acid-base electron exchange in the formation of 5- and 6-membered metal inhibitor ring complex. Polymeric complex was insoluble stable film formed through the process of complexation of the organic molecules on the copper surface.

FT-IR studies provide detailed information on the structure of the organic layer formed at the copper surface subsequent to exposure in potassium dodecanoate solution [23]. The results obtained with the use of FT-IR spectroscopy from copper samples treated in potassium dodecanoate solution indicate that the surface film formed on the copper consist mainly of cuprous oxide (Cu_2O) and copper dodecanoate species. Thus, the copper surface is being covered with cuprous oxide with an organic layer on top of it. FT-IR spectra of the synthesized copper dodecanoate showed existing of different bands: asymmetric and symmetric (CH_3), asymmetric and symmetric (CH_2), asymmetric and symmetric (COO^-) carboxylate stretches. Infrared spectra of carboxylic acids showed that the carboxylate ion has strong antisymmetric and relatively strong symmetric stretch absorptions. Relative positions of the asymmetric and symmetric carboxylic bands can be used to shed light on the type of carboxylate-to-metal complexation structure in a given metal carboxylate. FT-IR spectroscopy indicated the formation of a copper binocular complex with symmetrically bound carboxylate groups via a bridging bidentate divalent structure.

Sherif et al. [25] reported on the formation of the protective layer on the copper surface in 3,5%NaCl solution with addition of synthesized 5-(Phenyl)-4H-1,2,4-triazole-3-thiol (PTAT) and confirmed that PTAT molecules was strongly adsorbed on the copper surface using FT-IR technique. FT-IR spectra was recorded after immersion of copper electrode in a solution of 3,5%NaCl + 1000ppm PTAT for 16 days. Present peaks pointed to heterocyclic N-H band, CNH bending absorption band, absorption N-C=N band, and C-H vibration band. It has also been reported that the absorption band is either due to the presence of Cu in the scratched film from the copper surface as a result of a formation of PTAT-Cu(I) complex and/or due to PTAT-Cu(I)-H_2O complex.

The interaction between tetrazole derivates and the metal surface have been intensive studied [4]. Tetrazole derivates which were been used: 5-mercapto-1-methyl-tetrazole, 5-mercapto(Na salt)-1-methyl-tetrazole, 5-mercapto-1-acetic acid (Na salt)-tetrazole, 5-mercapto-1-phenyl-tetrazole, 5-phenyl-tetrazole and 5-amino-tetrazole in the 0,1M NaCl solution. Results obtained in the experiments showed that the presence of the additives on the metal surface was evident. The interaction of 5-phenyl-tetrazole was occurred through the existence of C=N group. C-S and N=N bands were evident on the 5-mercapto-1-phenyl-tetrazole. It can be assumed that the efficiency of the inhibitor may be due to the interaction of the anion with the copper surface or with the copper ions, giving the stable complex. Position of the phenyl group, -NH_2 group, -SH group in the heterocyclic ring can influence on the formation and efficiency of the protection coatings on the metal surface.

Hoque et al. [33] investigated the formation of stable self-assembled monolayers of 1H,1H,2H,2H-perfluoro-decyldimethylchlorosilane (PFMS) on an oxidized copper surface. Fourier transform infrared reflection/absorption spectroscopy (FT-IRRAS). Facts which were obtained in his paper point to coordination of the PFMS silicon atom with a cuprate molecule on the oxidized copper substrate. For PFMS/Cu, the absorption peaks for C-F stretching modes are found on the FT-IRRAS spectra. This invention concerned the presence of a perfluorinated alkyl chain film for PFMS/Cu. Results unambiguous indicated that the PFMS/Cu SAM was chemisorbed onto the oxidized Cu surface via a siloxy-copper (-Si-O-Cu-) bond. Results also indicated the presence of $Cu(OH)_2$ and absence of –SiO-groups on oxidized Cu before reaction with PFMS, and presence of siloxy groups and absence of $Cu(OH)_2$ on PFMS/Cu.

Lusk and Jennings [45] reported about formation of self-assembled monolayer in the presence of sodium S-alkyl thiosulfates. The structure of SAM on copper surface was examined using infrared spectroscopy. Special attention was directed to the effect of the chain length on the SAM effectiveness. Facts were been presented indicate that SAM formed with longer chain length has better protective properties than SAM formed with shorter chain length. Best result gave chain with 14 carbons in structure of the SAM.

QUARZ CRYSTAL MICROBALANCE STUDIES

Interfacial processes at electrode surface require utilization of sophisticated techniques in order to obtain detailed information on structure and composition of interfaces. Quarz crystal microbalance is one of the new and very useful methods applied in the electrochemical field. Electrochemical quartz crystal microbalance (EQCM) is a term for quartz crystal microbalance (QCM) when QCM is used in electrochemical cell. Quartz crystal microbalance consists of a thin quartz blade between two metal electrodes, which produce an alternating motion of the crystal at its resonant frequency. This frequency is very sensitive to mass changes of the crystal and its deposited electrode. EQCM was often used to note mass changes at electrode surface [46,47]. Sauerbrey's equation is commonly used to describe the linear relationship between the frequency shift (Δf) and the mass change (Δm):

$$\Delta f = -2,264 \times 10^{-6} F_0^2 \Delta m / S \qquad (7)$$

Where F_0 is the fundamental resonance frequency (Hz), $\Delta m/S$ is the surface mass change per unit area (gcm^{-2}). Corrosion rate determined by EQCM can be given by:

$$v_{corr} = \frac{\Delta m}{M \Delta t} = \frac{K_m \Delta f}{M \Delta t} \qquad (8)$$

where v_{corr} is the corrosion rate of metal per unit area, M is the atomic weight of metal, Δt is the total time during the potential scan /47/.

Electrochemical quartz crystal microbalance has a valuable part to play in the interpretation of corrosion and corrosion inhibition mechanism /48/, and it was often used to observe effect of some organic compounds on the metal surfaces in the aggressive environmental. The high sensitivity of quartz crystal microbalance is the basis for its application in thin film studies /46/.

Telegdi et al. [46] investigated inhibition effectiveness of some organic compound in different pH range. Organic compound which they used were: di-benzyl-sulfoxide (DBSO), di-phenyl-sulfoxide (DPSO), di-p-tolyl-sulfoxide (DPTSO), 5-mercapto-1-phenyl-tetrazole (5-McPhTT), 5-benzylidene-2,4-dioxotetrahydro-1,3-thiazole (5-BDT), 5-(4-isopropylbenylidene)-2,4-dioxotetrahydro-1,3-thiazole (5-IPBDT). These compounds were examined in acidic solution. In neutral media were examined ortho-chloro-benzo-hydroxamic acid (o-Cl-BHA), para- chloro-benzo-hydroxamic acid (p-Cl-BHA), para-nitro-benzo-hydro-xamic acid (p-N-BHA), o-methyl-benzo-hydroxamic acid (o-M-BHA). Results indicated that the best inhibition efficiency in the acidic media has DBSO. In the presence of 5-McPhTT a 2-D type layer was formed on the metal surface. QCM measurement showed a increase in the electrode mass which was a result of inhibitor adsorption. The addition of 5-IPBDT produced slight better protection than 5-BDT. This can be due to the presence of isopropyl group in 5-IPBDT, providing longer chain. 5-IPBDT was also chemisorbed on the electrode surface. Comparison between o-Cl-BHA and p-Cl-BHA using EQCM showed the influence of substituent position on the inhibition effect. The improved inhibition of p-Cl-BHA was not only due to delocalized electron distribution but also due to elongated chloro-benzo chain. EQCM measurements showed that copper dissolution followed a transport-limited mechanism, the rate of which was determined by copper diffusion. The strong decrease in copper dissolution in the presence of p-Cl-BHA because of protective power of the complex layer formed.

Bayoumi et al. [30] investigated kinetics interaction of BTA with the surface of copper in the salt water. The corrosion of copper in the salt water is a very complex process. During this process many soluble and insoluble products can be formed: $CuCl_2^-$, $CuCl_2$, $CuCl$, Cu_2O, $Cu_2(OH)_3Cl$ [49,50]. EQCM study point to attachment of BTA molecule on the electrode surface. During the adsorption of BTA on the copper surface investigators noticed three regions. Region I was attributed to the formation of the complex Cu(I)BTA. Region II was attributed to further attachment of BTA on the copper surface. The BTA that was attached

on the copper surface in the region II was involved in one or both of the following process: formation of more of the protective complex Cu(I)BTA, via outward diffusion of Cu^+ ions through the Cu(I)BTA film that formed in region I; Attachment of BTA on the Cu(I)BTA film, via physical adsorption without forming Cu(I)BTA. Results clearly showed further attachment of BTA on the copper surface to reach a plateau (regionIII) indicating attachment of an equilibrium thickness of the film.

In the another investigation was found that BTA was chemisorbed and formed a [Cu-BTA]$^+$ complex at the electrode surface. The inhibitory effect of BTA on the copper may be due to the adsorption of the complex at active sites where it might accept an electron from the cathode, and at the same time discharged copper atoms might already incorporate at the active sites [47].

Fonsati et al. [48] reported the results obtained by using EQCM in the study of copper corrosion in 0,1M NaCl solution in the absence and presence of some organic inhibitors. 2,4-dimercapto-pyramidine (DTU), 5-mercapto-1-phenyl-tetrazole (5McPhTa), benzotriazole (BTA), 1H,1,2,3-triazole [4,5b] pyridine (PyTz) were examined like inhibitors. Results showed that Δm values were the results of an algebric sum of different processes: adsorption of inhibitors and formation of surface film, solid surface compounds formation and soluble compounds dissolution.

SURFACE-ENHANCED RAMAN SPECTROSCOPY INVESTIGATION

Surface-enhanced Raman spectroscopy (SERS) has been established to be a useful technique in the characterization of adsorbates at interfaces [51]. Specifically, molecular information such as bonding, identity and orientation of adsorbed species may be elucidated from surface-enhanced Raman spectra. The intensity of the signals in the SER spectra is proportional to the number of scatterers on surface [52]. SERS measurements were carried out in order to characterize the species adsorbed at the electrode surface and their effect on the electrode dissolution [7,29,53]. SERS studies indicate that the identity of the molecule adsorbed to the surface is potential dependent [54].

Loo et al. [52] investigated surface-enhanced Raman spectra of benzotriazole (BTA) and 6-tolytriazole (6-TTA) mixtures on Cu electrode and found that the spectral features of the BTA and 6-TTA are very similar indicating that both molecules were adsorbed to the copper in a similar way. The bands in the region 1000-1600cm^{-1} for components Cu/BTA and Cu/6-TTA showed small differences in the frequency shift. Several bands in the region below 1000cm^{-1} were significance different from each other. Concentration of BTA and 6-TTA has significant importance on the mixture SER spectra. When the concentration of 6-TTA was more than BTA, the electrode surface was predominantly covered by the 6-TTA molecules. When BTA was predominant species in the solution on the Cu surface was predominant BTA molecules. Results point to that 6-TTA was strongly adsorbed on the copper surface than BTA. This is consequence of less soluble of 6-TTA than BTA.

Huynh et al. [29] examined the nature and orientation of the species adsorbed on the metal surface. The Raman spectrum of film on the copper surface of alkyl esters of 4- and 5-carboxybenzotriazole was examined. All inhibitors had very strong bands assigned to the C=O stretch, alkyl side chain bands and most of the benzene ring bands were either decreased in intensity or were absent in the SERS spectrum. Weak peaks assigned to the formation of N-H deformation mode. This indicated that the triazole ring is close to the copper surface. SERS spectra indicated that the alkyl ester molecules interact with copper surface through an azole ring nitrogen lone pair of electrons, and also experience physical adsorption with the copper through the hydrocarbon chain.

Vilamil et al. [53] reported about effect of sodium dodecylsulfate (SDS) on the copper dissolution in 0,5M H_2SO_4 and at 527cm^{-1} observed peak which indicates the presence of Cu_2O on the copper surface. In the presence of SDS peak had less intensity, suggesting dissolution of Cu_2O. SERS spectrum clearly showed that SDS was adsorbed onto copper surface. In the solution with SDS the C-H symmetric stretching mode of the SDS splits into two components, at 2874 and 2934cm^{-1}. Band at 2962cm^{-1} was caused to the C-H anti symmetric stretching. Vilamil et al. [53] also used SERS measurements to examined copper surface in 0,5M solution of sulphuric acid with addition of BTA and in the presence and absence of SDS. In the both case at 528cm^{-1} was observed peak witch indicating presence of Cu_2O. On the surface of metal developed $[Cu(I)BTA]_n$ polymeric layer. When the SDS was present in solution Cu_2O signal was importance weaker and $[Cu(I)BTA]_n$ signal had almost disappeared. $[Cu(I)BTA]_n$ signal was stronger at more positive potential. The main characteristic feature of the BTA species is the δ(NH) in plane bending mode at 1120 cm^{-1}. Therefore, one can conclude that at positive potentials benzotriazole adsorbs on copper forming a polymeric film, the $[Cu(I)BTA]n$, and at negative potentials one of the adsorbed species is the BTA molecule. Results of SERS spectra showed that in the presence of BTA, SDS was also adsorbed on the copper surface taking part of the passive film. SDS was adsorbed forming ion pairs with the BTA^+_2 species on the metal surface.

Yang et al. [28] explained formation of self-assembled monolayers of inositol hexsaphosphate onto copper surface. The features of IP_6 layer were evaluated by the time-dependent Raman spectroscopic measurement. The types of molecules studied for SAM formed on the copper surface in the previous studies are alkanethiols [55] and mercapto-alkanols [56].Yang et al. [28] showed the bands around 222 and 300cm^{-1} which originate from the copper oxide species. Band around 1612cm^{-1} showed adsorption of H_2O on the copper surface. The spectra recorded in the early stages of the formation of IP_6 layer on the copper surface confirmed that a prior to the formation of the IP_6 monolayers, firstly a chemically self-cleaning process occurred to remove some oxides species of copper from the top layer of the roughened copper surface via producing the soluble Cu_x-IP_6 complexes. IP_6 molecules were chemically adsorbed onto the freshly exposed copper surface to form the ordered monolayers through two co-planar phosphates.

Huynh et al. [7] used SERS measurements to confirm that the esters inhibit copper corrosion process by chemisorption of the protonated species ($CBTAH^+_2$-OE) on the metal surface through azole nitrogen. Van der Waals` forces of attraction between adjacent octyl chains oriented away from the copper surface were reliable to the increase of inhibition at low pH. SERS also suggest that at higher pH chemisorption was replaced by the deposition of a sterically hindered polymeric complex which was not protective as chemisorbed $CBTAH^+_2$-OE.

Huynh et al. [43] investigated a series of alkyl esters (methyl, buthil, hexyl, octyl) derived from carbo-xybenzotriazole like corrosion process inhibitors in Na_2SO_4 solution in the different pH range. It was proposed that the protonated species ($CBTAH^+_2$-R) was chemisorbed on the copper through an azole nitrogen and at low pH inhibition efficiency was determined by Van der Waals' forces of attraction between adjacent alkyl chains oriented away from the copper surface, which were increased with the length of the alkyl chain. On the contrary it was proposed that at high pH a polymeric complex was formed and steric hindrance acts to make the film less protective.

SCANNING TUNNELING MICROSCOPY MEASUREMENTS

Scanning tunneling microscopy has a great usage in the observing of the metal surface, in the underlying atomic scale processes. This method gave detailed about surface structure and morphology of the surface [57]. This new technique provides real 3D images of solid surfaces at a great resolution [38]. STM is also used to determine a formation of protective layer on the metal surface. Results obtained using STM indicated that formation of BTA protective layer was dependent upon surface orientation and anions present in solution particulary Cl⁻ [57]. BTA geometry adsorption was very interesting for some scientist and they used STM measurements in theirs investigation [58]. Scanning tunneling microscopy combined with conventional electrochemical techniques was used to determine the kinetics and mechanism of β-brass dealloying. STM images after dealloying showed the development of an irregular surface which attains a stationary regime [37].

Cho et al. [58] tried to solve the controversy of the BTA nature between non-adsorption and adsorption on the clean copper surface. STM measurements was used in this experiment and found that BTA molecules did adsorb on the clean copper surface with a well-ordered superstructure. Results indicated that BTA molecules were adsorbed randomly on the oxygen-induced area. BTA molecules coalesced together and made a cluster-like form with the increase of the BTA surface coverage. This cluster-like island became bigger with higher coverage, and after some time the whole surface was covered with a multilayer film.

Vogt et al. [44] investigated adsorption of BTA on copper electrode in 0,1M HCl and found that at higher potentials come to the formation of a thick, protective Cu(I)BTA film on the copper surface. Earlier studies showed that at negative potentials come to the chemisorption of BTA on the Cu [59-61] and at higher potential

come to the formation of a polymerized Cu(I)BTA complex [19,60]. In the HCl solution with addition of BTA was observed that the two maxima correspond to two individual adsorbates rather than to different parts of a single BTA molecule. STM results clearly indicated the presence of chemisorbed BTA layer on the Cu surface. BTA molecules were occupied well-defined adsorption sites. The apparent center of the two BTA molecules must be located on different adsorption sites within the unit cell. Observed adlayer structure was a compromise between well-defined BTA adsorption sites and maximum density. Influence of the anions on the structure of the chemisorbed BTA was small. Chemisorbed BTA layer was displaced by the Cl⁻ adlayer at -0,6V. At positive potential than -0,2V STM images become foggy. Also STM image was foggy after complete formation of the Cu(I)BTA layer. This was consequence of the poor electrical conductivity and the large thickness of the film. In HCl solution a direct conversion of the chemisorbed BTA phase into the polymerized Cu(I)BTA phase was reported. This was not possible when the Cl⁻ adlayer was formed. In the solution when was formed Cl⁻ adlayer on the Cu surface Cu dissolution could proceed in the same way as in the HCl solution without BTA. Cu dissolution was been inhibited by formation of Cu(I)BTA film. Film formation started with the production of $CuCl_2^-$. These ions reacted with BTA in the solution to Cu(I)BTA, which subsequently precipitates on the Cu surface and thus forming the inhibitive layer. In the initial stage of this process surface of copper was completely covered with Cl⁻ adlayer. This adlayer was been replaced by the Cu(I)BTA layer.

Polewska et al. [57] investigated anodic dissolution of copper and surface structure of copper in the pure 0,01M H_2SO_4 solution and in H_2SO_4 solution with BTA. After experiments they were found that in the pure H_2SO_4 solution a complex sulfate adlayer structure was formed. STM images indicated that BTA adsorbated species were adsorbed in the potential regime of the ordered sulphate adlayer, where they replaced sulphate adlayer. BTA adlayer was highly defective, and inhibited dissolution of copper. At more anodic potentials in the BTA adlayer was formed some defects, resulting in a roughening of the copper surface.

ENERGY DISPERSIVE X-RAY, X-RAY
DIFFRACTION AND X-RAY PHOTOELECTRON
SPECTROSCOPY STUDIES

Energy dispersive X-ray is technique which gives very useful information about surface structure [62]. Energy dispersive X-ray analysis gave additional information about inhibition mechanism. Corrosion inhibition process was associated with formation and growth of insoluble stable film on the copper surface through the process of complexation of the organic molecules [2].

The X-ray diffraction (XRD) method can be used not only for identification of crystalline phases in corrosion products [63] but also for their quantitative phase analysis based on measuring the intensity of a single diffraction line or even all the lines in the pattern. XRD measurements sometimes were not successful because of the small crys-

tallinity of the material, or because that the formed film was very thin [2]. X-ray photoelectron spectroscopy (XPS or ESCA) is nowadays one of the essential tools in the field of surface science. By applying XPS quantitatively to an alloy surface, we can estimate the composition and thickness of the surface film and the composition of alloy surface under the surface film without causing any serious damage to the specimen [64]. XPS has high sensitivity to surface along with nondestructive, quantitative, and state analytical characteristics, which are suitable for the surface analysis of such specimens as thin films formed in solution, i.e., passive films on stainless steels and amorphous alloys. AES (Auger electron spectroscopy) is an analogous technique from the viewpoint of analyzing depth /64/. The escape depth of a photoelectron is approximately proportional to the square root of its kinetic energy and is not strongly dependent on the substance which the photoelectron passes through. This means that XPS gives information of only the thin surface region of substance. The absolute sensitivity of XPS will be of the order of about 0,1% and all elements are detectable except hydrogen. If an alloy specimen has a surface film such as oxide film formed by reaction with the atmosphere and if its thickness is not too large as compared with the photoelectron escape depth, the XPS spectrum of the specimen will give peaks originated from both the alloy itself and the surface film on the alloy. In such a case, it is possible to determine simultaneously both the compositions of the surface film and the substrate alloy and also the thickness of the surface film using a certain assumption [65,66] without applying any etching technique. Since the thickness of a surface film depends on combination of material, environment, and other factors, this nondestructive method is not always applicable to the determination of film thickness and substrate alloy composition. Stress corrosion cracking (SCC) is rather a localized phenomenon and the conventional XPS is not likely to be suited for its study because of its low spatial resolution. However, since SCC susceptibility of metals and alloys is considered to be closely related with the properties of the surface films formed in the environment, the analysis of surface film by XPS may be able to contribute to SCC study. Conventional XPS is capable of giving nondestructively compositions of surface film and underlying alloy surface and also thickness of the surface film when the film thickness is not more than 10 nm [64].

Sherif and Park [42] used EDX measurements to investigate adsorption of AETDA molecules onto copper surface in Cl⁻ solution. During the experiments was observed that was formed two different areas on the copper surface. At the first area AETDA molecules were strongly adsorbed on the Cu surface with ability to prevent formation of cuprous chloride and oxychloride complexes onto metal surface. At the second area EDX spectra showed a lower content of AETDA and a higher content of Cu, indicating that only thin film of AETDA was formed. Those differences between areas indicated a smaller inhibition efficiency of AETDA.

Sherif [40] investigated copper surface in NaCl solution in the absence and in the presence of ATD. In the solution without ATD completely surface of Cu was covered with corrosion products. The EDX spectrum give

information that on the Cu surface existing CuCl, CuCl$_2^-$, Cu$_2$O and/or Cu$_2$(OH)$_3$Cl. EDX analysis of the copper surface in the Cl$^-$ solution with ATD indicated that the ATD molecules were strongly adsorbed on the copper surface.

Sherif and Park [6] investigated the influence of the ATD on the formation of the protective layer on the Cu surface in the HCl solution. EDX spectrum showed that on the Cu surface were located 77,3%C, 8,42%N, 9,71%O, 1,30%S, 2,01%Cu and 1,28%Cl. Those results indicated that on the Cu surface was formed Cu-ATD protective layer. 2,5-dimercapto-1,3,5-thiandiazole and 2-mercapto-5-methyl-1,3,4-thiadiazole had similar structure like ATD, and formed self-assembled monolayers on the metal surface [67]. SEM experiments also indicated that AETD molecules had been strongly adsorbed on the copper surface forming Cu-AETD bonds [6].

Sherif and Park [3] investigated adsorption of N-phenyl-1,4-phenylenediamine (NPPD) on the copper surface in 0,5M HCl solution. The inhibition of copper corrosion by NPPD in 3%NaCl solution was carried out and was found that NPPD was a good inhibitor with strong adsorption on the copper surface [68]. NPPD molecules were adsorbed on the metal surface and a formed a complex with the soluble copper complex CuCl$_2^-$ on the metal surface. SEM experiments showed two morphologically different spots. EDX results for the first spot showed atomic composition of 74%C and 7,59%N. Those results indicated that NPPD might be oxidized. The low Cl and Cu contents indicated that the copper surface was covered by the adsorbed NPPD molecules and/or Cu(I)-NPPD protective complex. Also, Cu(I)-NPPD complex was formed on the copper surface at area II and it suppress copper dissolution

Lalitha et al. [16] investigated copper surface in acidic solution in the absence and in the presence of 1,2,4 triazole derivates (3-amino 1,2,4-triazole; 3-amino 5-mercapto 1,2,4-triazole; 3-amino 5-methylthio 1,2,4-triazole) and in the presence of ionic surfactants cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS). In the uninhibited solution XRD spectra showed presence of Cu$_2$O, CuO and CuCl species. In the solution with 3-amino 5-methylthio 1,2,4-triazole and CTAB protective non-porous film was formed and CuO was vanished. Also, protective layer was formed in the solution containing 3-amino 5-methylthio 1,2,4-triazole and SDS.

Abelev et al. [23] followed formation of protective layer of potassium dodecanoate in sulfate solution. Protective layer was characterized using XPS and FTIR measurements. First spectrum was registered from copper surface subsequente to 1h exposure at 0,2V$_{SCE}$ in 1g/l K$_2$SO$_4$ solution with 0,07M potassium dodecanoate. The peak at 285eV on C 1s spectra points to C-C or C-H binding, peak at 286,2eV points to C-O binding and peak at 288,6eV points to COO$^-$ binding originating from carboxylate species on the surface. On the O 1s spectra authors obtained peak which point to formation of Cu$_2$O at 530,6eV. The main peak in Cu 2p$_{3/2}$ spectrum at a binding energy of 932,7eV assigned to Cu$_2$O, metallic copper, or both species. The second peak at O 1s and Cu 2p$_{3/2}$ spectra point to

formation of Cu(II) species bonded with a dodecanoate chain through a carboxylate group at the copper surface. The C 1s spectrum of copper dodecanoate contents three peaks. First peak at 285eV attributed to a C-C or C-H binding. The second peak attributed to C-O binding, and the third peak assigned to a C=O binding. The O 1s spectra contents one main peak attributed to oxygen in carboxylate group, while the second peak indicates on adsorbed water. In the Cu 2p$_{3/2}$ spectra the main peak at 934,9eV was attributed to the Cu^{2+}. The second peak was attributed to the Cu$_2$O.

Sinapi et al. [69] followed formation of n-dodencanethiol (DT), 3-mercaptopropyltrimethoxysilane (MPTS) and 11-perfluorobutylundecanethiol (F$_4$H$_{11}$) monolayers on the Cu surface. The analyzed core-level lines were calibrated against the C 1s binding energy characteristic of aliphatic carbons conventionally set at 285,0eV. Covered surface has been characterized by XPS and contact angle measurements. Those measurements showed that modification take place through thiolate bonds, converting the Cu(II) surface into copper oxide Cu(I) and leaving-CH$_3$, -Si(OMe)$_3$ or –(CF$_2$)$_3$CF$_3$ terminal functions pointing out at the surface. Cu 2p line was present in all cases (Cu$_{DT}$, Cu$_{MPTS}$, Cu$_{F4H11}$) corresponded to the underlying copper substrate. Carbon signal C 1s was seen with a higher intensity on specimens modified by molecules with long alkyl chains. S 2p spectra of Cu$_{DT}$, Cu$_{MPTS}$, Cu$_{F4H11}$ contain peak at 162,5eV which indicate formation of thiolate bonds Cu-S-. MPTS molecule made two reactive functions (-SH and –Si(OMe)$_3$), but the thiol group was the one which react with Cu surface in order to form self-assembled monolayers. On the C 1s spectra of Cu$_{DT}$ one main component which attributed to the aliphatic carbon atoms of the DT backbone was seen. The small component at 286,2eV is typical of alkoxy functions (C-O-C) which are likely due to physisorbed atmospheric pollutants or to the formation of copper ethoxide species due to the solvent used. In the earlier works [70,71] was found at 285,0eV methylene groups of the propyl chain HS-(CH$_2$)$_3$-Si(OMe)$_3$ and at 287,0eV methoxy groups of the terminal function HS-(CH$_2$)$_3$-Si(OMe)$_3$. This confirms bonding of the MPTS molecules on copper surface by the thiol groups. XPS measurements showed that the underlying copper substrate is in the Cu(I) oxidation state after modification by each of the three molecule. Note that before any treatment, a layer of CuO and Cu(OH)$_2$ was found on samples surfaces evidencing a Cu(II) chemical state of copper (spectra not shown here). The 'removal effect' of Cu(II) species by the reducing thiol functions has already been made clear and discussed in previous works [72,73].

Hoque et al. [33] investigated formation of stable monolayer on oxidized copper surface via reaction with 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane (PFMS). XPS measurements were used to analyze structure, chemical composition and stability of self-assembled monolayers onto metal surface. Measurements showed that the PFMS/Cu SAM was chemisorbed onto the oxidized Cu surface via a siloxy-copper (-Si-O-Cu-) bond. Chlorosilane were rapidly hydrolyzed by water and form silanols:

$-Si\text{-}Cl + H_2O = -Si\text{-}OH + HCl$ (9)

Perfluorodecyldimethylsilano; undergoes a condensation reaction with copper hydroxide present on the oxidized Cu surface to form a siloxy-copper bond:

$C_8F_{17}(CH_2)_2(CH_3)_2Si\text{-}OH + OH\text{-}Cu\text{-} =$
$= C_8F_{17}(CH_2)_2(CH_3)_2Si\text{-}O\text{-}Cu\text{-}$ (10)
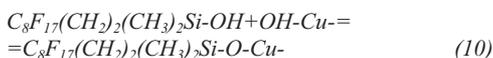
The peak component at the binding energy of 283.8 eV can be attributed to SiCHx which arises from the 1 methylene (-CH$_2$-) and 2 methyl (-CH$_3$) groups coordinated with Si in the alkyl chain of the PFMS molecule. The binding energy at 284.8 eV is assigned to CHx which arises from the 1 non-Si coordinated methylene (-CH$_2$-) present in PFMS molecule and a small amount from adventitious carbon contamination. The high binding-energy peaks of 291.1 and 293.3 eV can be unambiguously attributed to the difluoromethylene (-CF$_2$-) and –CF$_3$ functional groups, respectively, present in the perfluoroalkyl chain of PFMS. XPS data collected at different places on the PFMS/Cu surface indicate the formation of a chemically uniform perfluoroalkyl film on the oxidized Cu substrate. These results clearly lead to the conclusion that a perfluorinated alkyl chain film was present for both untreated and treated PFMS/Cu. XPS was capable of resolving neutral copper, copper with valence of +1 and copper with a valence of +2 through the analysis of the core level Cu 2p peaks and their corresponding "shakeup satellite". In the 2p region the most pronounced satellite peak was for Cu(II). The peak due to CuO assigned at 934eV was shifted to higher energy by 1,1eV from Cu and Cu$_2$O peaks. The peak at energy 935,1eV was associate with Cu(OH)$_2$ which was shifted 1,1eV from the CuO peak on the high-energy side. Cu(OH)$_2$ was formed on the surface at some point between oxidization and silanization of Cu. After reaction with PFMS, two distinct peaks appeared whichb corresponding to metallic Cu and Cu(I), confirmed presence of Cu(I) for PFMS/Cu. Once the PFMS molecule has been hydrolyzed, a silanol (-Si-OH) forms and HCl is produced as a byproduct. At this point in the reaction, it is quite possible that PFMS can dimerize to form bis(perfluoro-decyldimethyl)disiloxane [F$_3$C(CF$_2$)$_7$(CH$_2$)$_2$-(CH$_3$)$_2$Si-O-Si(CH$_3$)$_2$(CH$_2$)$_2$(CF$_2$)$_7$CF$_3$], which can physisorb onto the oxidized Cu surface. The PFMS/Cu film stability against harsh treatments can be explained by the hypothesis that silanol is capable of reacting with copper hydroxide (-CuOH) on the substrate surface, then the similarity between the siloxane bond (-Si-O-Si-) and the siloxy-copper bond (-Cu-O-Si-) proposed above becomes obvious. Thus, this peak in the Si spectrum at 102.6 eV can be a direct indication that such a bond has formed for PFMS/Cu. The O 1s lines (upper) at 529.8, 530.8, and 531.7eV are attributed to CuO, Cu$_2$O, and Cu(OH)$_2$, respectively. The lack of the CuO peak indicates that Cu(II) has disappeared after modification with PFMS. The disappearance of the CuO and Cu(OH)$_2$ peaks for PFMS/Cu supports further the conclusion that a siloxy-copper bond has formed as already stated above. The robustness of the PFMS/Cu SAM film can be attributed, at least in part, to the formation of a siloxy-copper bond (-Si-O-Cu-) after reaction of PFMS with the oxidized Cu substrate. This conclusion is based upon XPS and FT-IRRAS data indicating the presence of copper hydroxide (Cu(OH)$_2$) and absence of siloxy (-SiO-) groups on oxidized Cu before reaction with PFMS, the presence of siloxy groups and absence of copper hydroxide on PFMS/Cu, and the resistance of PFMS/Cu to harsh treatments.

Zhang et al. [74] investigated formation of Cu$^+$MBI complex film on the copper surface in the 0,5M H$_2$SO$_4$ solution with 2-mercapto benzimidazole. Also, they investigated synergistic effect of MBI and iodide ions on copper corrosion in H$_2$SO$_4$. It is well known that Cu inhibitors such as BTA, MBT can form an inhibitor film consisting of either a (Cu$^+$BTA) or a (Cu$^+$MBI) complex on the copper surface [61]. Protective film can block the dissolution of copper as well as the active site of oxygen reduction. Wu et al. [75] proposed that the effect of iodide ions in improving the inhibition efficiency of BTA worked by improving the adsorption of BTA$^+_2$ on the copper surface and forming a new Cu (IBTA) complex film through a covalent bond between BTA and iodide ions. XPS measurements were performed in H$_2$SO$_4$ solution containing MBI (MBI/Cu) and MBI+KI (MBI+KI)/Cu. N 1s peak and S 2p peak which were observed indicated that MBI film was present on the surface of the copper in the both solution. Interaction between copper and MBI goes across N and S atoms. O 1s peak may be attributed to oxygen in H$_2$O, inorganic sulfate, and oxides of copper. Potassium and iodide didn't participate in the formation of surface film on the Cu. The Cu 2p3/2 band for Cu in the both solution indicated that Cu was mainly present in the cation form. Also, was observed that cupric oxide didn't exist on the samples surface. XPS results show that the iodide ions do not participate in the formation of the (Cu$^+$MBI) inhibitor film. The synergistic effect may result from initial contact adsorption of iodide anions on the copper surface, thereby facilitating the adsorption of protonated MBI and the formation of a (Cu$^+$MBI) inhibitive film.

Mekhalif et al. [32] investigated Cu surface in 0,5M HClO$_4$ solution with 12-(N-pyrrolyl)-n-dodecanethiol, and found that on the copper surface come to formation of protective monolayer. SAMs of bifunctional molecular connectors have been shown to influence the deposition of thick films of electroactive polymers and improve their adhesion, uniformity, density and morphology [76-78]. XPS measurements of bare Cu substrate and modified with PyC$_{12}$SH were performed. Cu 2p line was present in the both cases, corresponding to the underlying copper substrate. In the case of bare Cu substrate the C 1s and O 1s levels were present corresponding to carbon contaminants and oxidized species respectively. The C 1s line for bare copper had a main peak attributed to the aliphatic carbons of adsorbed atmospheric contaminants, and another peak at 289,2eV typical of oxidized carbon species of the type CO-O-C and CO-O-H. In the case of modified copper substrate the peak at 285,9eV was due to carbons linked to the nitrogen atom of the pyrole cycle, while the peak at 285,0eV originated from the other carbons in PyC$_{12}$SH. On the surface didn't exist or exist in the very small number carbon oxidized species of the type CO-O-C and CO-O-H. The peaks at 933,8eV and 569,6eV on the Cu 2p$_{3/2}$ and

Cu_{LMM} correspond to the presence of the CuO and $Cu(OH)_2$ layer on the copper surface. XPS results indicated that thiolate species were present at the copper/organothiol interface. O 1s analyses of bare copper substrate indicated that on the copper surface exist copper oxidized species: CuO, Cu_2O and $Cu(OH)_2$. XPS measurements were performed in the NaOH and NaCl solutions and were found that N 1s, S 2s and S 2p lines were notable which pointed to the presence of $PyC_{12}SH$ on the substrate at the end of the electrochemical cycle. Results also indicate that Cu_2O species were present on the Cu substrate.

Sinapi et al. [72] investigated formation a two-dimensional polymer film of hydrolyzed 3-mercaptopropyl-trimethoxysilane on Cu surface. The analyzed core level lines (C 1s, O 1s, S 2p, Si 2p, F 1s, Cu 2p and Cu_{LMM}) were calibrated with respect to the C 1s binding energy conventionally set here at 285.0eV and characteristic of aliphatic carbons. Results had shown that MPTS chemisorbs on Cu surface through strong thiolate bonds forming a well-organized self-assembled monolayer able to decrease the corrosion of the underlying copper substrate. Formed film was been characterized by X-ray photoelectron spectroscopy. C 1s line revealed the various types of carbon environments: methylene groups in the propyl chain and methoxy groups. O 1s region had single sharp peak which corresponding to methoxy head groups $HS-(CH_2)_3-Si(OMe)_3$. Hydrolysis of the terminal functions of the modified substrate is source of drastic changes in XPS spectra clearly evidencing the development of a Si–O–Si framework. Methoxy groups in the C 1s region had almost disappeared leaving a single peak at 285,0eV standing for aliphatic carbon. The O 1s region had one main peak at 523,3eV which was at 532,8eV before hydrolysis. This shift to lower binding energy was consistent with the cleavage of –Si-OCH$_3$ bond during the hydrolysis process. The main oxygen peak was accompanied by two additional characteristics referring to Cu_2O and to H_2O rationalized respectively by oxidation resulting from partial cleavage of the C–S bonds of the MPTS monolayer during hydrolysis and by the adsorption of water molecules at the siloxane surface after hydrolysis. Another effect of the chemical transformation of the modified substrate's surface was the displacement towards lower binding energy of the Si 2p level marking the conversion from –Si(OMe)$_3$ to Si–O–Si. After hydrolysis, the methoxy head groups form cross-linkages laterally leading to a thin siloxane network across the surface supported by an alkanethiol film. This siloxane film contains a small number of residual hydroxyl groups at the surface providing a –SiOH-containing environment predisposed to undergo further chemical modification of the surface and suggesting many uses for these films. Sinapi et al. [72] demonstrated that if MPTS coverage has the ability to inhibit corrosion in the presence of water, the two-dimensional double layer exhibits dramatic improvements in protection of the underlying copper substrate with only a modest increase in thickness of the self-assembled film.

Souto et al. [79] investigated adsorption of ethyl xanthate on copper surface in moderately alkaline aqueous solutions. XPS data suggest that copper protection is achieved through the growth of a cuprous diethyl dixanthogen layer on the metal in which the oxidation state +1 of copper becomes stabilized. Finally, the active role of ethyl xanthate ions in the formation of a complex chemisorbed film on copper, which is responsible for the corrosion resistance of the metal, can be concluded from the observation of an S sp signal at 162.5eV, which is clearly displayed above the background signal.

CONCLUSION

Based on previously displayed information, it can be conclusion that a large number of copper corrosion inhibition act via adsorption on metal surface and complex formation. Protective film can block the dissolution of copper as well as the active site of oxygen reduction. The inhibition efficiency of the protective film was strongly dependent on the degree of its polymerization. EIS measurements results show that the protective film formed on the metal surfaces become more protective as the alkyl chain made longer. Film coverage is also a good index of the inhibition efficiency. The increase of film coverage can reflect the increase of the number of the molecules adsorbed on metal surface and the improvement of the inhibition effect.

FT-IR spectra pointed to formation of bonds between molecules which indicated to the chemisorption of inhibitors on the metal surface through nitrogen atom. Polymeric complex can be formed by covalent and coordinate covalent bonds. The interaction of tetrazole derivates are occurred through the existence of C=N group. It can be assumed that the efficiency of the inhibitor may be due to the interaction of the anion with the copper surface or with the copper ions, giving the stable complex. Position of the phenyl group, -NH$_2$ group, -SH group in the heterocyclic ring can influence on the formation and efficiency of the protection coatings on the metal surface.

SERS measurements indicated that the alkyl ester molecules interact with copper surface through an azole ring nitrogen lone pair of electrons, and also experience physical adsorption with the copper through the hydrocarbon chain. Some molecules are chemically adsorbed onto copper surface and form ordered monolayers.

Potential have influence on the formation of the protective film on the metal surface. At positive potentials benzotriazole adsorbs on copper forming a polymeric film, and at negative potentials come to the chemisorption of BTA on the Cu surface. Protonated species in the numerous cases $(CBTAH^+_2-R)$ was chemisorbed on the copper through azoles nitrogen.

The EDX spectrum give information that on the Cu surface existing CuCl, $CuCl_2^-$, Cu_2O and/or $Cu_2(OH)_3Cl$ in the solution without inhibitors. Corrosion products mostly disappeared in the solution with inhibitors.

A different type of bonds is recognized on the copper surface in the solution which contents some inhibitor. Measurements showed that the PFMS/Cu SAM was chemisorbed onto the oxidized Cu surface via a siloxy-copper (-Si-O-Cu-) bond. MPTS is chemisorbs on Cu surface through strong thiolate bonds forming a well-

organized self-assembled monolayer able to decrease the corrosion of the underlying copper substrate.

Acknowledgements

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