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3 **The First X-Ray Photoelectron Spectroscopy Surface Analysis of 4-methyl-2-phenyl-imidazole**
4 **Adsorbed on Copper**
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13
14 **Abstract**
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17 The focus of this article is a detailed surface analytical study by X-ray photoelectron spectroscopy
18 (XPS) of 4-methyl-2-phenyl-imidazole (MePhI) adsorbed from 3 wt.% NaCl solution on a Cu surface. It
19 is shown for the first time that MePhI is a Cu corrosion inhibitor in chloride solution after short-term
20 (1-100h) and long-term immersion periods (180 days), and that MePhI is an anodic-type corrosion
21 inhibitor. Surface analysis was first performed by examination of the Cu surface layer chemical
22 structure, followed by surface layer thickness analysis according to the Tougaard method. It is shown
23 that a very thin layer is formed. Next, a detailed angle-resolved XPS analysis was performed to study
24 the manner of MePhI bonding on the copper surface. It is claimed that the MePhI molecule connects
25 to the surface via C and N atoms. A flat orientation of MePhI molecules, parallel to the copper surface,
26 is suggested.
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31 *Keywords:* Copper, Surface Analysis, XPS, Corrosion Inhibitor, 3D-Profilometry, Polarisation Resistance
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1 Introduction

The main focus of this work is on the surface analytical study of a specific organic compound, 4-methyl-2-phenyl-imidazole (MePhI, Fig. 1), adsorbed on copper substrate in order to explain molecule bonding to the Cu surface. This article also describes how this compound was used for the first time to protect any metallic material against corrosion. Herein copper is considered. In fact, the corrosion inhibition ability of MePhI was proven after 1-100h of immersion. Moreover, high corrosion inhibition effectiveness was also proven after 180 days of immersion, which is an uncommonly long-term immersion period in corrosion inhibitor studies.

Currently, as a result of corrosion related problems, the total annual estimated direct cost of corrosion in the U.S. is \$276 billion, which is approximately 3.1% of the US Gross Domestic Product.¹ Corrosion cannot be completely prevented, but there are effective ways to mitigate it. One of the most convenient methods is the employment of corrosion inhibitors. A corrosion inhibitor is a chemical compound that is dissolved in a corrosive medium, which in a certain way adsorbs on the surface and provides corrosion protection. The corrosion inhibitor mechanism is in most cases not understood, because it is usually only empirically determined that a given inhibitor works for a particular metal in a certain solution by trial and error experiments. Typically, after the determination of corrosion inhibition ability, surface analysis of the employed compounds is not performed.

Industrially, copper is one of the most important nonferrous materials, due to its long life. It is frequently utilized in water distribution networks. However, if exposed to chloride-containing solutions it needs to be protected against corrosion, where corrosion inhibitors can be employed.²

To study corrosion inhibitor surface phenomena highly sensitive surface analytical techniques are required, as the corrosion inhibitor surface layer thickness is usually only a few monolayers thick.³⁻⁶ In studying such phenomena, X-ray photoelectron spectroscopy (XPS) is a powerful technique for obtaining information about the surface chemistry of the adsorbed compounds and the manner of bonding at the adsorbate-metal interface.^{3, 5, 7, 8} The drawback of this procedure is that possible contamination from the surrounding atmosphere can adsorb on the surface after sample preparation (during drying and sample transfer to the spectrometer). One needs to be aware of this when interpreting the XPS spectra.^{9, 10} On the other hand, XPS analysis provides specific information that is difficult to obtain by means of other instrumental techniques. For example, using the XPS method, we demonstrated that benzotriazole (probably the most well-known Cu corrosion inhibitor) adsorbs on the oxidized copper surface and forms a Cu(I)-benzotriazole complex.⁹ By reconstruction of the X-ray-excited Auger spectra, we established a method for determining the oxide layer thickness below the corrosion inhibitor surface layer. We showed that benzotriazole reduces the thickness of the oxide layer formed on Cu in chloride media compared with the thickness of the oxide layer formed on the same material in the same solution, but without benzotriazole inside.¹⁰

Herein, a compound that effectively protects copper from corrosion in a highly corrosive chloride solution will be presented. First, corrosion inhibition effectiveness will be proven electrochemically and by topography measurements. Moreover, a corrosion inhibitor type will be proposed (either a cathodic-, anodic-, or mixed-type inhibitor). Second, the manner of bonding will be studied by the XPS technique. The studied compound, MePhI, is – to the best of the author's knowledge – presented here for the first time as a potential copper corrosion inhibitor. In this study, a 3 wt.% NaCl solution is selected as a corrosion medium, because it is highly corrosive to copper and therefore an attractive medium to impose the worst case scenario in terms of copper corrosion.^{11, 12} Industrially, copper is usually exposed to a lower chloride content medium.

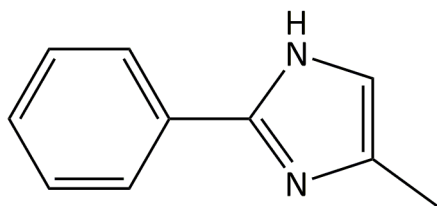


Fig. 1: The chemical structure of MePhI.

2 Experimental

2.1 Sample and solution preparations

MePhI was purchased from Sigma Aldrich, USA (with a purity of 95.0 wt.%) and NaCl from Carlo Erba, Italy (pro analysis). MePhI was dissolved in aqueous 3 wt.% NaCl solution that was prepared with Milli-Q water, which has a resistivity of 18.2 MΩ cm.

A copper plate of 99.999 wt.% Cu (temper half hard) provided by Goodfellow (Cambridge, UK) were cut out in the shape of discs 15 mm in diameter to create Cu samples 2 mm thick. These samples were used for the electrochemical, profilometry, and XPS measurements. The first stage of sample cleaning was performed by grinding. This procedure also serves to make a uniform Cu surface in every analysis. Using a rotating device, the specimens were ground under a stream of water, starting with 1000-grit SiC paper and continued with 2400- and 4000-grit papers (provided by Struers, Ballerup, Denmark). Between each paper change, the sample was rinsed with Milli-Q water to remove the particles resulting from grinding. Samples were ground in one direction until all imperfections were removed and the surface was covered with a uniform pattern of scratches. The grinding direction was changed four times, with the sample turned 90° each time to minimize abrasion. Before each analysis, surfaces were checked under a microscope and if any scratches were still present the preparation procedure was repeated. After grinding, the samples were cleaned ultrasonically in a bath of 50% ethanol/50% Milli-Q water (by volume) and afterwards thoroughly rinsed with Milli-Q water. The same procedure as described previously was used.^{9, 10, 13-24}

2.2 Electrochemistry

Cu working electrodes were embedded in a Teflon holder using a Teflon o-ring. These Teflon parts were purchased from Princeton Applied Research (PAR). The area exposed to the solution was 1 cm². The experiments were performed in a three-electrode cell (volume 1 L) closed to air under stagnant conditions at 25 °C, controlled by a thermostat. A saturated calomel electrode (i.e. SCE, 0.2444 V vs. SHE) was used as a reference electrode, along with a platinum mesh as a counter electrode. The reference electrode was inserted in the Luggin capillary. Measurements were carried out with a Gamry 600™ potentiostat/galvanostat controlled by a Gamry Framework program. Porous glass frits (PAR G0300) were employed for the reference electrode and Luggin capillary.

Polarisation resistance measurements were performed during 100 h of immersion, i.e. after 1, 3, 5, 10, 30, 50, and 100h of immersion. Experiments were performed in the potential range ±5 mV vs. E_{ocp} . A potential scan rate of 0.1 mV/s was used. The R_p values were determined by fitting the measured potential (E) vs. current density (j) data to a straight line using Gamry's EChemAnalyst software. The slope of this line represents R_p . This procedure was used rather than determining R_p as the derivative of the $E-j$ curve at E_{corr} , where $j = 0$ ($R_p = (dE/dj)_{j=0}$).^{13, 25}

Potentiodynamic curve measurements were carried out after 100h of immersion using a potential scan rate of 0.1 mV/s. Measurements started at -0.25 V vs. the open circuit potential, E_{oc} , and continued with increasing potential in the anodic direction until the signal reached a current response of 1 mA cm⁻² (no current limitation was set for the non-inhibited solution). Three replicate measurements were performed. As no significant difference in the potentiodynamic behaviour (measured curves overlapped) was observed, one of the three measurements is presented in the figure below.

2.3 3D-profilometry

Surface analysis of the samples immersed for 180 days in 3 wt.% NaCl solution with or without 1 mM MePhI was performed with a profilometer, namely a Form Talysurf Series 2 (Taylor-Hobson Ltd.) under laboratory conditions, i.e. on average 23 °C. This profilometer has a lateral resolution of 1 μm and a vertical resolution of approximately 5 nm. The 3D-profile is acquired by measuring the surface profile in one direction, then the next measurement starts in the same parallel direction, but 1 μm apart. The measured data are then processed with TalyMap Gold 4.1 software to calculate the mean surface roughness and to create a surface profile. To level the profile, corrections were made to exclude general geometrical shape and possible measurement-induced bad fits.^{13, 14, 16}

2.4 X-ray photoelectron spectroscopy

For the XPS analysis, the samples underwent Cu immersion in 1L of 3 wt.% NaCl containing 1 mM MePhI. After 1h of immersion, the samples were taken from the solution, rinsed thoroughly with Milli-Q water, dried with argon gas, and immediately transferred into the XPS instrument, where the analysis was performed. To check for repeatability, three sample analyses prepared in the same way were performed. There was no significant deviation in the peak shapes and position between these three measurements, therefore we can consider the spectra in Figs. 4-6 to be representative.

XPS measurements were carried out with a PHI 5700 spectrometer using an Al K_{α} standard and monochromatic X-ray radiation sources ($h\nu = 1486.6$ eV). The energy of the emitted photoelectrons was analysed with a hemispherical electron analyser operating at pass energies of 29.3 eV and 58.7 eV for high-resolution spectra and 187.8 eV for survey spectra. The base pressure in the spectrometer was $2 \cdot 10^{-10}$ mbar. Analyses were performed at emitted photoelectron take-off angles (θ) of 5°, 20°, 45°, and 90° with respect to the sample surface. Spectra measured at different angles will differ due to the different analysed depths as the analysing region is composed of the inhibitor surface layer, copper oxides, and metallic copper, i.e. it is inhomogeneous in depth. The analysed depth by the XPS method is a function of the take-off angle, $3 \cdot (\text{IMFP}) \cdot \sin(\theta)$. The IMFP is the inelastic mean free path. The analysed depth is defined as the depth from which 90% of the XPS signal originates. In the present case, the analysed depth was in the range of 0.5 – 8.0 nm by taking into account the IMFP value of 2-4 nm (see below Section 3.4.3). The XPS analysed area radius was 0.4 mm. The C 1s adventitious carbon peak at a binding energy (E_B) of 284.8 eV was employed to correct the energy scale of the XPS spectra and possible charging effect. The data were processed with MultiPak software (version 8.1C) for Shirley²⁶ or linear background subtraction (in the case of the Cu 2p line²⁷). The accuracy of the E_B scale is estimated to be 0.2 eV. Different features in the XPS spectra, such as pure core-level transitions (Cu 2p, C 1s, O 1s, and N 1s), as well as the X-ray excited Auger Cu $L_{3,4,5}M_{4,5}$ peak, were analysed. As a reference, a sputter-cleaned Cu sample was employed. Sputtering of the sample surface was performed with a 1 keV Ar⁺ ion beam rastering over an area of 4 by 4 mm.^{9, 10, 17, 18, 22, 23} MePhI solid chemical (powder) was also analysed and used as a reference to compare it with the MePhI-treated Cu samples. A third reference was the X-ray excited Cu $L_{3,4,5}M_{4,5}$ spectrum representing Cu₂O in order to compare it with the X-ray excited Cu $L_{3,4,5}M_{4,5}$ spectra for the MePhI-treated Cu (section 3.4.3). This measurement was taken after rinsing and drying the Cu sample, which was previously immersed in pure 3% NaCl for 1h. For that sample, it was shown that only Cu₂O was present and no CuCl remained on the surface and CuCl₂, CuO, and Cu(OH)₂ were not formed (as explained in detail in refs. [^{9, 10}]).

3 Results and discussion

3.1 Polarisation resistance measurements

The R_p value is a measure of how a metal resists transferring an electron to the electroactive species in solution. It is a convenient method for quickly determining if a particular compound in a certain medium acts as a corrosion inhibitor or not. The higher this value is the more resistant the system is against general corrosion. R_p measurements were repeated until all values fitted into Grubbs statistical tests (outliers were discarded²⁸) and the average values were calculated for 3 wt.% solution with or without 1 mM MePhI. From these average R_p values the inhibition effectiveness of the MePhI inhibitor was calculated according to Eq. 1.^{21, 29}

$$\eta = \frac{R_p(\text{MePhI-containing solution}) - R_p(\text{solution without MePhI})}{R_p(\text{MePhI-containing solution})} \times 100 \quad (1)$$

The calculated η after 1, 3, 5, 10, 30, 50, and 100h of immersion was 83.5, 93.2, 97.1, 98.7, 98.9, 98.4, 98.9%, respectively.

3.2 Potentiodynamic curve measurements

Potentiodynamic curves for Cu in 3 wt.% NaCl solution with or without 1 mM MePhI after 100h of immersion are shown in Fig. 2. A relatively long immersion time before performing potentiodynamic curve measurements was employed in order for the Cu in the corrosive medium to achieve a steady state.³⁰ In order to avoid the capacitance effects if higher scan rates were to be applied and so that the current/voltage relationship only reflects the interfacial process at every potential of the polarization scan, the measurements were carried out at a low potential scan rate of 0.1 mV/s.^{16, 22, 23, 30, 31}

By initiating the measurement in the cathodic region, the potentiodynamic behaviour of Cu in 3 wt.% NaCl solution is first governed by a hydrogen evolution reaction (as this is a slightly acidic medium with a pH of around 5.5) and mass-transport-controlled reduction of dissolved oxygen (absorbed in the solution from the atmosphere). At potentials more positive than E_{oc} , Cu starts to oxidize. At the primary passivation potential, E_{pp} , the linear relationship between $\log i$ and E is no longer present, because CuCl_2^- activity exceeds its solubility equilibrium and the formation of CuCl film starts to predominate.^{16, 32}

By comparing curves for Cu in the non-inhibited system and for the system containing 1 mM MePhI, in the cathodic region, there is no significant difference in the potentiodynamic behaviour. Therefore, MePhI does not have an influence on the hydrogen evolution reaction or oxygen reduction. However, the E_{oc} (designated in Fig. 2) is transferred to more positive potentials in the MePhI-containing solution compared to the measurement in non-inhibited solution.

In the anodic region, at potentials more positive than E_{oc} , the potentiodynamic curve for MePhI-containing solution is transferred 1-2 orders of magnitude to the lower current densities (i) compared to the measurement in the non-inhibited solution. This implies that MePhI inhibits copper oxidation. MePhI can therefore be classified as an anodic-type inhibitor. This is also confirmed by the fact that E_{oc} for the inhibited system shifts to more positive potentials.

Hitherto, to the best of the author's knowledge, it is herein shown for the first time that MePhI can be considered to be a corrosion inhibitor for Cu in 3 wt.% NaCl solution in the initial stage of its immersion in a corrosive medium. Next, a longer-term immersion period will be considered in topography measurements (see below).

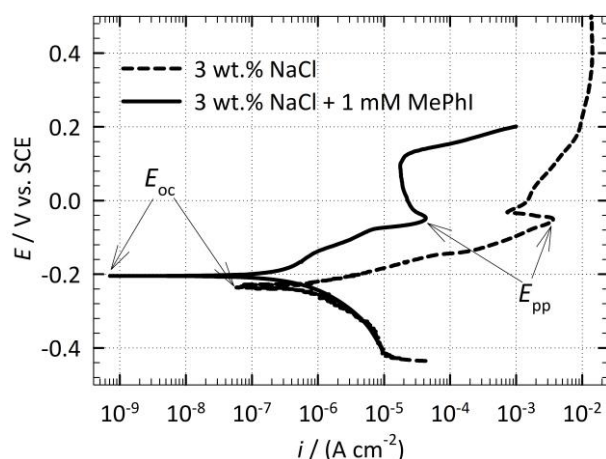


Figure 2: Potentiodynamic curve measurements of Cu in 3 wt.% NaCl solution with or without 1 mM MePhI.

3.3 Topography measurements

Fig. 3 shows 3D-profiles measured for copper surfaces immersed for 180 days in 3 wt.% NaCl solution with or without 1 mM MePhI, thoroughly rinsed with Milli-Q water, and dried under a stream of nitrogen. Three replicate measurements were performed for Cu immersed in solution with or without 1 mM MePhI (only one of each profile is shown in Fig. 3). Clearly, the sample immersed in non-inhibited solution (without MePhI) has a much rougher surface compared to the sample that was immersed in solution containing MePhI. This proves that MePhI is effective in preventing copper corrosion also after a relatively long-term immersion period. To quantify surface roughness, the mean surface roughness (S_a), which is based on general surface roughness, was calculated according to Eq. 2. L_x and L_y in Eq. 2 represent the acquisition lengths of the surface in the x and y directions, and $z(x,y)$ is the height.^{13, 14} For this calculation, TalyMap Gold 4.1 software was employed. The average S_a value (out of 3 measurements) for the sample immersed in non-inhibited solution was 1.21 μm , and for the sample immersed in the solution containing 1 mM MePhI it was 0.181 μm . For comparison, an average S_a after the copper preparation procedure (see Section 2.1) is 8 nm. Furthermore, the S_a values measured after performing the same experiment (immersion in inhibited 3 wt.% NaCl for 180 days) in solutions containing 1 mM 2-mercaptobenzoxazole²² or 1 mM 2-mercaptobenzimidazole¹⁶ or 100 ppm 2-mercaptobenzothiazole²³ (a lower concentration of 100 ppm compared with a 1 mM concentration of 2-mercaptobenzoxazole and 2-mercaptobenzimidazole due to limited solubility) were 0.125 μm , 0.160 μm , and 0.085 μm , respectively. Therefore, only slightly lower corrosion inhibition effectiveness of MePhI is found compared to the 3 compounds tested previously, which are some of the most effective for Cu in chloride medium.

$$S_a = \frac{1}{L_x} \frac{1}{L_y} \int_0^{L_x} \int_0^{L_y} |z(x,y)| dx dy \quad (2)$$

For a corrosion inhibitor it is very important to understand how the molecules bond and orient on the metallic surface – in order to be able to propose its inhibition mechanism. Based on such motivation, next a surface analytical study was performed for MePhI adsorbed on a Cu substrate (see below). The interpretation of XPS results can reveal one part of the overall MePhI corrosion inhibition mechanism and therefore represent motivation for further analysis.

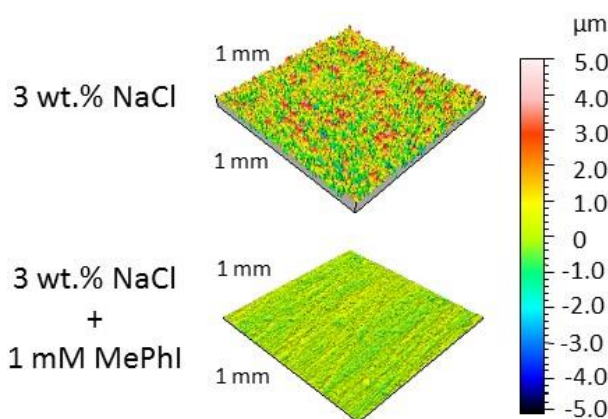


Fig. 3: 3D-profiles of Cu samples after 180 days of immersion in 3 wt.% NaCl with or without 1 mM MePhI.

3.4 XPS measurements

3.4.1 Chemical structure on the Cu surface

Before performing an XPS analysis, a number of facts need to be taken into account. Being thermodynamically favourable, copper oxidizes when exposed to an open atmosphere or in aqueous solution. In the present case, copper is exposed to an open atmosphere or aqueous solution during sample preparation, drying, exposure to 3 wt.% NaCl solution, and transfer to the spectrometer. Therefore, copper oxides are expected to be present on the surface. It is also common in the present experimental procedure that adventitious atmospheric species (most frequently carbon-containing molecules or their oxidized products) adsorb on the Cu surface during sample preparation, drying, and transfer to the spectrometer. This is usually called adventitious carbon or sometimes contamination. Moreover, it was determined previously that 1h of immersion of a Cu sample in a corrosion inhibitor-containing solution is sufficient to study molecules bonding on the metallic surface. By employing longer-term immersion or higher concentrations, thicker surface layers (most likely crystallites¹⁴) were sometimes observed and the excitation source did not reach the substrate, making the XPS analysis less useful.^{9, 17, 18, 22, 23} Due to this reason, XPS analysis was performed for the Cu sample immersed for 1h in 3 wt.% NaCl solution containing 1 mM MePhI. The sample was then rinsed with Milli-Q water and dried under a stream of Ar.

Fig. 4 shows the survey spectrum for the MePhI-treated Cu (the upper spectrum). The lower spectrum in Fig. 4 represents the sputter-cleaned Cu surface attained by argon-ion bombardment until the surface was free of N, C, S, and O signals and is presented here for comparison. A clear indication that MePhI molecules were adsorbed on the Cu substrate is the presence of N 1s and C 1s signals for the treated sample as N and C atoms are present in the MePhI molecule. However, C 1s can also originate from other carbonaceous species, which can adsorb from the atmosphere (contamination). A peak representing Cl on the surface is missing (it is expected to be present at an E_B of about 200 eV¹⁸). Previously, it was reported that Cl compound is incorporated in the azole surface layer.³³ However, in the present case we can exclude the presence of chlorine-containing compounds in the MePhI surface layer on the Cu surface. Moreover, no other peaks that would represent species beside MePhI on the surface were detected. Therefore, as a chemical of 95 wt.% purity was employed, it can be concluded that impurities possibly present in the purchased MePhI chemical did not adsorb and subsequently did not affect the adsorption of the MePhI compound.

Cu 3s, Cu 3p, X-ray excited Auger Cu $L_3M_{4,5}M_{4,5}$, and Cu 2p peaks for the upper spectrum in Fig. 4 represent metallic copper, Cu₂O, a Cu-inhibitor complex (see below the X-ray excited Auger Cu

$L_{3}M_{4,5}M_{4,5}$ analysis), or a combination of all three. The presence of CuO and $Cu(OH)_2$ on the surface can be excluded based on the $Cu\ 2p$ spectra (see below). $CuCl$ and $CuCl_2$ species are also not present on the surface as no Cl signal was detected. The origin of the $O\ 1s$ peak can come from Cu_2O , water, or oxidized carbonaceous atmospheric species, which can adsorb on the surface during sample drying and transfer to the spectrometer.

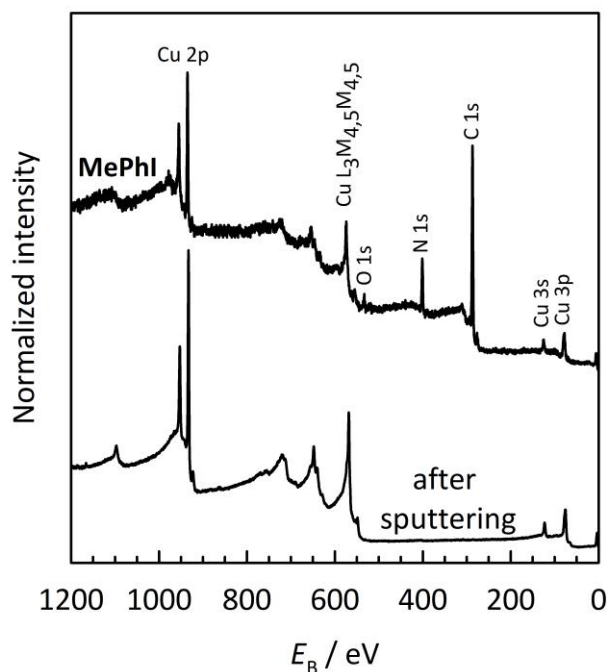


Fig. 4: XPS survey spectra measured at $\theta = 45^\circ$ of the MePhi-treated (the upper spectrum) and sputter-cleaned Cu (the lower spectrum).

3.4.2 Determination of the thickness of the MePhi surface layer

The thickness of the MePhi surface layer was estimated with the method developed by Tougaard.^{34, 35} This method is based on the fact that the background signal in the XPS spectra results from inelastically scattered electrons originating from the subsurface region and travelling towards the surface. In the present case, the part of the survey spectrum on the high binding energy side of the X-ray excited Auger $Cu\ L_{3}M_{4,5}M_{4,5}$ peak is taken into account for such analysis. Using this method, the background curve is modelled by changing the surface layer thickness value (therefore, this is an input parameter). The resulting theoretical background curve is adjusted to the measured spectrum until satisfactory agreement of the adjusted spectra with the measured spectra is obtained and the background contribution is eliminated to obtain the background corrected spectrum (Fig. 5). In this procedure a simple structure consisting of an organic over-layer on the substrate is considered.

Another piece of information needed is the IMFP value for the $Cu\ L_{3}L_{4,5}M_{4,5}$ transition at a kinetic energy of 920 eV. This parameter for MePhi-treated Cu is not exactly known and it is difficult to obtain with the required accuracy. Herein, it is estimated based on previous knowledge and references. An IMFP value of 2.96 nm was previously employed based on the reference database³⁶ (by taking into account the formation of an organic over-layer). This value was employed before for inhibitor surface layer thicknesses determination on Cu.^{9, 17, 18, 22} Moreover, two limiting IMFP values of 2 nm and 4 nm were also taken into account to estimate the uncertainty (error). These IMFP values were also previously reported for certain organic molecules adsorbed on metal surfaces.³⁷⁻⁴¹

Herein, for the MePhi-treated Cu the surface layer thickness was determined to be 0.3 nm by employing an IMFP of 2 nm (Fig. 5a) and 0.5 nm by employing an IMFP of 4 nm (Fig. 5b). Due to such a

thin inhibitor surface layer, analysis for an IMFP of 2.98 nm was not performed (the inhibitor surface layer thickness would then be between 0.3 nm and 0.5 nm). On that basis, it can be concluded that the MePhI surface layer thickness is 0.3-0.5 nm. Under similar experimental conditions as employed herein, inhibitor surface layer thicknesses were determined, using the same Tougaard method, to be in the range of 0.3–2.4 nm.^{9, 17, 18, 22, 23, 42} Therefore, the MePhI surface layer formed on Cu after 1h immersion in 3 wt.% NaCl containing the inhibitor is one the thinnest among corrosion inhibitors previously tested.

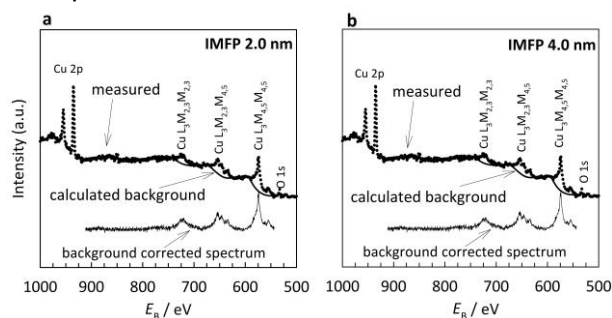


Fig. 5: Determination of the MePhI surface layer thickness by employing the Tougaard method^{34, 35}. The thickness of the MePhI surface layer as 0.3-0.5 nm was determined using IMFPs of 2 nm and 4 nm.

3.4.3 High-resolution XPS spectra analysis

Fig. 6 shows high-resolution XPS spectra measured at $\theta = 5^\circ$, 20° , 45° , and 90° . The analysed depth increases by increasing the θ , and vice-versa, it decreases by decreasing the θ , because analysed depth is a function of the θ , i.e. $3 \times (\text{IMFP}) \times \sin(\theta)$. Therefore, the topmost species can be detected and distinguished from the species present in the deeper subsurface regions by decreasing the θ , because the surface sensitivity increases and most of the signal comes from the topmost species. Herein, the signal obtained at θ of 5° and 20° should be taken into account only informatively as at θ lower than 30° there is a significant contribution of electron scattering on the surface. It is not necessary that they lose energy, but they do not leave the surface immediately as they change their path to the analyser. That is why their depth of origin is questionable.^{43, 44} Moreover, the precise determination of low θ in the instrument is also very difficult to achieve, thus contributing to experimental error when the analysed depth is under investigation. Moreover, at low θ , the signal-to-noise ratio is lower than at higher θ , because less signal is obtained.

Fig. 6a shows Cu 2p spectra with characteristic Cu 2p_{3/2} (at an E_B of approximately 952.5 eV) and Cu 2p_{1/2} (at an E_B of approximately 931.5 eV) peaks.⁴⁵ The shapes and position of these peaks for the sputter-cleaned Cu and MePhI-treated Cu at all θ do not differ significantly. The dashed lines represent the E_B at which shake-up satellites are expected, indicating the presence of Cu(II)-species on the surface. However, as these satellites are missing at that E_B for all θ , Cu(II)-species can be excluded from being present on the surface. Therefore, no CuO, Cu(OH)₂, or Cu(II)-MePhI complex (complexes of Cu(II) ions and N-containing molecules were reported previously⁴⁶⁻⁴⁹) are present on the surface. Thus, based on the Cu 2p analysis, only Cu(I)-species or metallic Cu can be on the surface. On the other hand, Cu 2p spectra analysis is not a suitable method for Cu(I)-species analysis as the peaks with a different Cu(I)-environment or metallic Cu are too close together in terms of E_B . For that case, it is more suitable to analyse the XPS-excited Cu L₃M_{4,5}M_{4,5} spectra shown in Fig. 6b. The XPS-excited Cu L₃M_{4,5}M_{4,5} spectrum for pure Cu (sputter-cleaned, the lowest spectrum in Fig. 6b) exhibits four peaks (labelled 1-4), with the most intense being peak 2. For comparison, the Cu₂O spectrum is also given, which shows a more intensely expressed peak 3 relative to peak 2. In the case of MePhI-treated Cu, the XPS-excited Cu L₃M_{4,5}M_{4,5} spectra at all θ show the most intense peak 4 relative to peaks 1-3 and are different

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3 compared to the spectra for pure Cu and Cu₂O. This characteristic feature was well documented before
4 to demonstrate that Cu(I)-inhibitor complexes (as no Cu(II)-species are present) were formed on the
5 surface.^{9-11, 17, 22, 37, 50, 51} On that basis, it can be concluded that a Cu(I)-MePhI connection was formed
6 on the surface.
7

8 The formation of Cu(I)-triazole complexes was reported before by Antonijević et al.⁵², who claim
9 that these complexes prevent the formation of CuCl₂⁻ (the second stage in the copper corrosion
10 process⁵³) and thus decrease the rate of corrosion. Cu(I) ions most likely originate due to Cu corrosion
11 in chloride solution.
12

13 High-resolution N 1s spectra are shown in Fig. 6c. There is no significant change in the shape and
14 peak position for all θ in the case of MePhI-treated Cu. The N 1s spectrum for the MePhI solid chemical
15 shows 2 peaks separated by 1.3 eV, implying two different N environments in the molecule (MePhI
16 contains two N-atoms in the molecule with a different environment, Fig. 1). Different N 1s spectra for
17 MePhI-treated Cu compared with the spectrum for MePhI solid chemical suggests that N atoms of that
18 molecule are involved in the surface bonding with the copper substrate or the formation of the
19 Cu(I)-MePhI connection (as explained above). As discussed above, measurements for θ less than 30°
20 are not reliable. Moreover, the N 1s spectra measured at 45° and 90° do not differ. This is most likely
21 due to the very thin surface layer, as confirmed above by the Tougaard thickness analysis to be 0.3-0.5
22 nm. The analysed depth at 45° and 90° is deeper than 0.5 nm (the analysed depth is calculated as
23 $3 \cdot (\text{IMFP}) \cdot \sin(\theta)$), therefore at these angles the excitation signal reaches all surface layers (MePhI, Cu₂O,
24 and Cu). Another explanation is that the molecules are lying flat on the surface and connection to the
25 surface goes through the π -electrons of the benzene and imidazole ring. A flat adsorption of azole-type
26 molecules (benzotriazol – one of the most well-known copper corrosion inhibitors¹¹) was already
27 proposed before by Cho et al.⁵⁴ by using scanning tunnelling microscopy. They claim that this molecule
28 forms a well-oriented superstructure corresponding to a flat adsorption scheme with π -d interactions.
29

30 The shapes and peak positions of the high-resolution C 1s spectra at all θ in the case of
31 MePhI-treated Cu are not significantly different (Fig. 6d), confirming the above statement regarding
32 the flat orientation. However, compared to the spectrum for MePhI solid chemical, these C 1s peaks
33 are wider at their FWHM (full width at half maximum) – 1.96 eV for MePhI-treated Cu and 1.34 eV for
34 MePhI solid chemical. Therefore, the involvement of C atoms in the MePhI surface bonding on Cu
35 cannot be excluded.
36

37 High-resolution O 1s spectra are shown in Fig. 6e. Compared to the signals representing Cu-, N-,
38 and C-species, the signal-to-noise ratio is lower for these measurements as a small amount of oxygen
39 atoms is present on the surface. As was also the case for the N 1s and C 1s spectra, the O 1s spectra
40 for the MePhI-treated Cu do not differ significantly at all θ . The centre of that peak is located at an E_B
41 of 531.6 eV. The location of the peak at an E_B of 530.6 eV was previously reported to correspond to
42 the formation of Cu₂O on the surface (below the inhibitor surface layer)¹⁷. Moreover, water molecules
43 remaining on the surface also cannot be excluded. The peak representing water according to the NIST
44 Standard Reference Database should appear at an E_B of 532.8-538.0 eV.⁴⁵ Therefore, by taking the
45 lower limiting E_B value, i.e. 532.8 eV, it can be claimed that the peaks for Cu₂O and water overlap as
46 the centre of the O 1s spectra is at their approximate middle E_B . Cu₂O and water molecules that are
47 hydrogen-bonded to the inhibitor surface layer and remain on the surface after sample drying was
48 previously reported also for other inhibitor-treated Cu samples.^{17, 18, 22, 23} There are no Cu(II)-species
49 (as proven by the Cu 2p spectra analysis, see above), therefore no CuO or Cu(OH)₂ are present on the
50 surface that could possibly contribute to the O 1s signal.
51

52 In summary, it is shown that the C and N atoms of the MePhI molecule are most likely involved in
53 the surface bonding and that no significant change in the position and shape of the peaks is observed
54 at different θ . According to the XPS-excited Cu L₃M_{4,5}M_{4,5} spectra, this connection is via Cu(I) ions. As
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discussed above, we cannot exclude the possible flat (parallel to the surface) orientation of MePhI molecules on the surface.

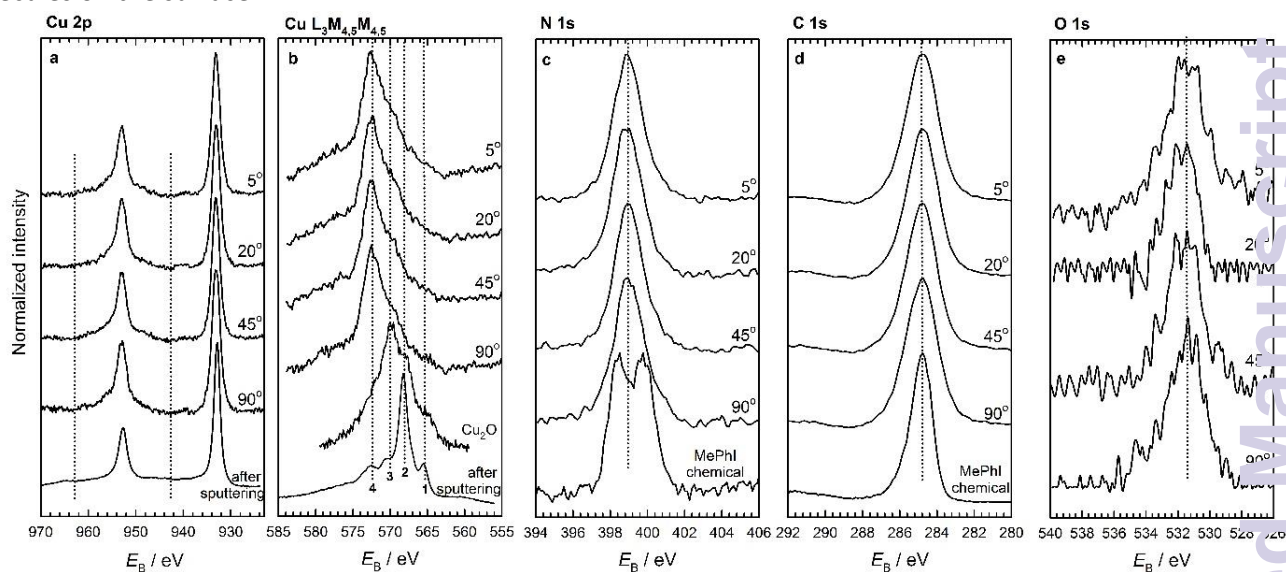


Fig. 6: Cu 2p, Cu L₃M_{4,5}M_{4,5}, N 1s, C 1s, and O 1s high-resolution spectra analysed at $\theta = 5, 20, 45,$ and 90° . The lowest curve represents the sputter-cleaned Cu sample (a and b) or MePhI solid chemical (c and d).

4 Conclusions

This study focuses on a surface analytical study of 4-methyl-2-phenyl-imidazole (MePhI) adsorbed on copper substrate from 3 wt.% NaCl solution. An electrochemical test and a 3D-profilometry analysis were performed to check if MePhI can be considered to be a copper corrosion inhibitor. Next, by X-ray photoelectron spectroscopy (XPS), surface analysis of the adsorbed MePhI on copper substrate from 3 wt.% NaCl solution (1h immersion) was performed.

Polarisation resistance measurements showed that MePhI is an effective corrosion inhibitor for Cu in 3 wt.% NaCl solution during 100h of immersion. The calculated inhibition effectiveness relative to non-inhibited solution was as high as 98.9%. Potentiodynamic curve measurements reveal that MePhI inhibits the anodic reaction of the corrosion couple, therefore it can be classified as an anodic-type inhibitor. Based on the topography measurements, the high corrosion inhibition effectiveness of MePhI was also proven after 180 days of immersion. Thus, it is shown for the first time that MePhI is a copper corrosion inhibitor in chloride solution.

XPS measurements showed that Cu(II)-species and chloro-containing compounds are not present on the Cu surface after Cu treatment in MePhI-containing solution. The thickness of the MePhI surface layer formed after 1h immersion is 0.3-0.5 nm, as confirmed by Tougaard thickness analysis. The XPS-excited Auger Cu $L_3M_{4,5}M_{4,5}$ spectra for the MePhI-treated Cu is attributed to the formation of a Cu(I)-MePhI connection. Angle-resolved XPS measurements suggests that both the C and N atoms of the MePhI molecule are involved in the inhibitor surface bonding. Finally, it is also suggested that MePhI molecules are lying flat on the surface.

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